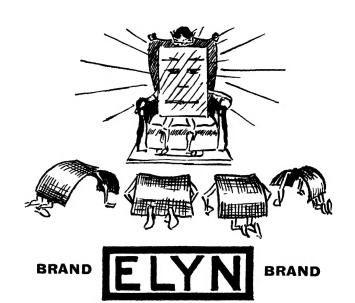
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# TIN AND THE TIN INDUSTRY

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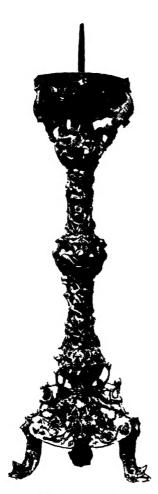
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THE GLOUCFSTER
CANDLESTICK
(Twelfth century)

A FLEMISH ALTAR
CANDLESTICK
(Seventeenth century)
Frontsspiece

(1463B)

# PITMAN'S COMMON COMMODITIES AND INDUSTRIES

# TIN

### AND THE TIN INDUSTRY

THE METAL HISTORY, CHARACTER
AND APPLICATION

BY

### A. H. MUNDEY



SECOND EDITION

LONDON
SIR ISAAC PITMAN & SONS, LTD.
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BATH, MELBOURNE, TORONTO, NEW YORK



### **PREFACE**

The immense wealth of scientific literature on the whole family of metals, available to the student, the manufacturer, and the man of commerce, is such that the author has considerable diffidence in introducing yet another addition to the store. But, although in the large treatises the purely scientific aspects of the metallurgy of tin, its chemical and physical character, and its uses in engineering, manufacture, and the arts are discussed in great detail, it is difficult to obtain, in an inexpensive and handy volume, a concise account of the chief facts of importance concerning a metal which must of necessity have some interest for everyone. It is to meet this need that this little volume is presented.

It is hoped that some of the technical matters may prove helpful to users of tin in its many applications, and that even when neither instruction nor technical information is sought or needed the review of some of the chief uses of this metal, so important in the history and commerce of our country, may prove of interest.

The author has drawn freely from standard works on metallurgy and the Journal of the Institute of Metals, and acknowledges with gratitude the kindness of many friends, particularly Messrs. Fry's Metal Foundry, for permission to use illustrations and descriptions concerning printers' alloys, antifriction metals, solders, and die casting; the Welsh Plate and Sheet Manufacturers' Association, for much information on tin plate; and Messrs. Venesta, Ltd., for help in the highly specialized industry in tin-foil and collapsible tubes.

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A CORNISH TIN MINE

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# TIN AND THE TIN INDUSTRY

#### CHAPTER I

#### EARLY HISTORY OF TIN

TIN is a metal which possesses an unusual amount of interest in our own country. Though by no means so important a metal as iron in respect to our national wealth and industry, it appears to have been the earliest of the known articles of export from Britain. The metal was known in very early times, but there was undoubtedly much confusion in the minds of the early philosophers with regard to it, or, what is more probable, the records of their observations were not made very clearly.

It is not quite certain whether the word "bedil" in the Old Testament really indicated the metal tin only, but this word was translated by the Latin *Stannum*, by which the present-day chemist and metallurgist knows the metal.

It is, however, fascinating to contemplate that those old merchant adventurers, the Phœnicians, made perilous voyages to these islands of ours to obtain tin, called in the Greek  $\kappa a\sigma\sigma i\tau\epsilon\rho\sigma s$ , and in the Arabic Kasdir. The islands in the Atlantic from whence it was obtained were called the Cassiterides, and the principal ore from which it is still obtained is known as cassiterite.

That the first name given to our land appeared to designate the Islands of Tin, and the first export a highly important metallurgical one, appears to be not only of extraordinary interest, but almost prophetic of the great part metallurgical science was to play in the life and industries of our land.

There appears to be ample evidence that the earliest known source of tin was Cornwall, and possibly the reference by Diodorus Siculus in describing the custom of the inhabitants in taking the tin from the mainland to a small island called Iktis, by a causeway which permitted communication at low water, but which at high tide was flooded, refers to St. Michael's Mount.

The fact is very important that the early experience of the mining operations for tin has been a great asset to the men of Cornwall, Devonshire, and South Wales, and to this day there seems to be hardly an important mining district in existence in which men from these districts have not had an active part in the work of development or management. This is no doubt due to the fact that tin mining has many points of similarity with the mining for gold and many of the rare metals.

Tin has been found in small quantities in the "native" state, that is, not combined with non-metallic elements, together with gold, in Siberia, Guiana, and Bolivia.

Oxide of tin SnO<sub>2</sub> is contained in a more or less pure form in the ore cassiterite, tinstone or black tin, which is the only ore of commercial importance. When pure it contains 78.6 per cent of tin. Its colour varies from brown to black. Its specific gravity is from 6.3 to 7.1.

The term black tin is usually applied to the concentrates obtained by dressing the ore, and contains from 65 to 70 per cent of tin.

Cassiterite occurs in veins or lodes and also in alluvial sands or gravel, in the form of rounded nodules and grains, and is in the latter case called "stream" tin, in which form the chief supplies of the world, those from the Malay Peninsula, Banca, and Billiton, occur.

#### EARLY HISTORY OF TIN

Tin is sometimes found in a complex ore called tin pyrites and as silicates, and has even been discovered in meteoric masses.

In Cornwall the veins or lodes occur in the granite and in clay slate beds, frequently in the border zones.

Tin mines exist in other parts of Europe, but on a less important scale than in Cornwall. As before stated, the chief supplies are from the Malay Peninsula and the neighbouring islands, but quite considerable quantities come from Bolivia, Australia, Tasmania, Burma, China, and Siam.

The world's tin production as given in Quinn's Metal Handbook for 1926 is—

	1923	1924	1925 1
	Tons	Tons	Tons.
Dutch Indies	27,808	30,000	31,000
Bolivia	28,683	29,447	30,500
Federated Malay States	37,649	44,043	46,000
Unfederated Malay States	2,056	2,500	2,500
Siam and Burma .	8,133	9,000	10,000
Nigeria	5,935	6,196	6,200
Australia	2,201	2,273	1,800
South Africa	875	1,245	1,000
Cornwall	1,021	1,986	2,500
China	8,568	7,434	8,000
Elsewhere	1,500	1,500	1,500
	124,429	135,624	141,000

The extraction of tin from the ore is almost always effected by dry processes, electrolytic and wet methods being confined to the extraction from tin-plate scrap or certain residues and by-products. The ore is first concentrated by hand picking and then by mechanical processes, washing and "dressing" and occasionally roasting.

Stream tin is hand-picked and then washed in sluices or on tables. When the ore is in lump form it is crushed

<sup>&</sup>lt;sup>1</sup> Estimated.

and washed. The high specific gravity of the tin-oxide facilitates the separation of the gangue or rocky material, as the stream of water washes the lighter material away.

Other impurities, however, frequently occur which cannot be removed by this simple process. Iron, copper, and arsenical pyrites and sometimes wolfram (a compound of iron, manganese, and tungsten) are present.

The treatment of ores containing these impurities varies with the character and condition of the impurity present. Wolfram, which is a heavy mineral, is removed as completely as possible by hand picking. The crushed ore is then roasted in a reverberatory furnace; during this operation it is constantly rabbled or turned over on the hearth, in order to expose fresh portions and surfaces to the oxidizing action of the air. The arsenical compounds are rapidly oxidized, arsenious oxide being produced, and it is obvious that to allow this substance, which is very volatile, to escape into the air by means of the chimney would be both dangerous and wasteful. Special means are, therefore, adopted to collect the fume. Very long flues or large suitably-designed condensing chambers are connected with the furnace, in which the fume of arsenious oxide sublimes or condenses, passing from the state of vapour directly to a solid deposit on the interior surface of the walls of the condensing chambers. It is called sublimation to distinguish it from the commoner process of condensation, when an intermediate or fluid state is obtained.

The sulphur present is also oxidized to sulphur-dioxide which is usually allowed to escape as there is insufficient to justify the provision of special apparatus for its further oxidation and conversion to sulphuric acid.

The iron and copper pyrites are occasionally roasted

at a low temperature to sulphates; it is then possible to dissolve and remove these by a subsequent washing or leaching process, but as a rule the oxidation is fairly complete and oxides of iron and copper are formed and are removed by simple washing.

The Wolfram which escaped the hand picking is unaltered. In order to remove this, Oxland devised a special operation. The ore is smelted with sufficient soda ash to convert all tungsten into tungstate of soda. This compound is soluble in water and the smelted ore is lixiviated or treated with water, removing the soluble oxides.

Loss of tin in this process and other objections, such as high cost and small demand for sodium tungstate, have led to its abandonment generally. The roasted concentrate is treated with diluted sulphuric acid and any remaining wolfram is removed by magnetic separators designed by Wetherill. Several ingenious mechanical tables have been devised to perfect the washing and economical separation of the impurities and waste products from the ore proper or concentrate.

Efforts to economize by saving labour in the roasting operation by the use of mechanically-worked furnaces have been employed. These are typified by the Oxland and Hocking furnace (see Fig. 1).

The powdered ore is introduced by the hopper (h) and passes down the revolving sloping tube (B), which is fitted internally with longitudinal ledges set radially, but not reaching the centre. Thus the ore as it trickles down is constantly turned over, at the same time meeting the heated gases and free atmospheric oxygen. The fire grate is shown at A with fire place H. The oxidized ore after its journey down the sloping tube drops into the funnel F and is afterwards withdrawn at f.

The sublimation or condensing chambers are seen, the walls of the chambers, as well as the baffles or separating walls, are smooth, so as to allow the ready removal of the sublimate of arsenious oxide, and the flue gases are compelled to take a serpentine course through the chambers, thus facilitating the cooling process and the deposition of the sublimate.

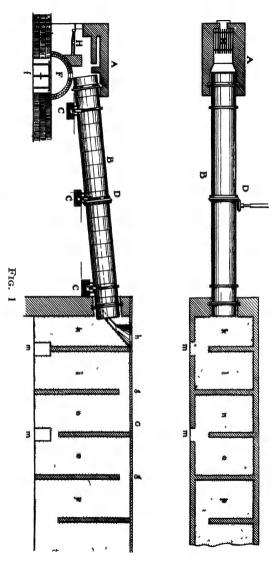
The difficulties in managing mechanical furnaces with economy have led to the abandonment of the Oxland and Hocking furnace to a large extent, in fact, it is stated that it is not in actual work anywhere at present. But the reintroduction of the principle is indicated by recent inventions; it is not unlikely that modern furnaces of this type will be in use again shortly.

The processes of extraction of the metal from the concentrate, after dressing, are—

- (a) Smelting, yielding crude tin.
- (b) Refining the crude tin.
- (c) Treatment of tin-bearing slags and residues.

The concentrate, or washed and roasted ore, usually contains from 60 to 70 per cent of tin. It is mixed with about one-fifth its weight of anthracite, moistened with water and charged on to the hearth of a reverberatory furnace. A certain amount of tin-bearing slags from former operations are included in the charge, together with fluxes such as lime and fluospar, to slag away the silicious matter.

The amount and character of the fluxes are controlled by consideration of the analysis of the ore and other constituents of the charge. The furnace construction is shown in the illustration (Fig. 2). The temperature is gradually raised almost to a white heat, the charge being stirred from time to time, and after about five hours the reduced metal is tapped out into an iron



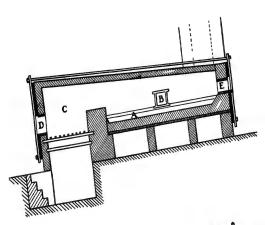
REVOLVING CALCINING FURNACE

metal-pot or kettle, which is separately heated. These metal pots communicate with the hearth of the reverberatory furnace by channels connected with the tapping hole.

The chemical reactions are simple, but the oxide of tin in the ore is reduced with difficulty. Much care and patience are necessary in addition to a very high temperature. The carbon of the anthracite combines with the oxygen of the tin-oxide, forming carbon-monoxide, which, turning to carbon-dioxide, passes up the flue, the liberated metallic tin remaining in the well of the furnace until enough has collected to justify tapping. The metal is ladled into ingot moulds. The metal is impure, owing to the presence of small quantities of other metals which have been reduced with the tin and become dissolved in it.

The refining operations vary in character; the first is called "liquation." The pigs or ingots of impure tin are placed upon the upper portions of the sloping hearth of a reverberatory furnace, which is so arranged that the temperature may be kept under strict control. It is never allowed to rise very much above the melting point of pure tin, as most of the impurities which are commonly present have a melting point much higher, and also form alloys which are less easily fusible than the pure metal. These undesirable substances are left behind upon the upper portion of the furnace hearth, while the readily fusible metal liquates or melts and runs out, down the sloping hearth, and escapes through specially designed channels and tapping holes into externally heated melting pots or kettles.

There still remain a certain amount of impurities which are not capable of removal by the liquation process. These are removed by the double operations of "poling" and "tossing."



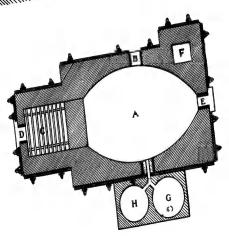


FIG 2

# REVIRBERATORY SMELTING FURNACE

- A Furnace hearth
  B Door
  C Fire place and grate
  D Door for clearing fire place
  F Door for rabbling charge on hearth
  F Flue
  G & H Metal pots or kettles

Poles of green wood are thrust into the molten metal and kept beneath the surface, and the distillation of the wood at the temperature of the fluid bath of metal causes the disengagement of gases and water vapour, which agitate the metal, and bring to the surface dissolved impurities, when they are oxidized by the oxygen of the air, and are subsequently skimmed off. This operation is termed "poling," and the name may be regarded as fairly indicative. The second or "tossing" process is also aimed at the final elimination of impurities by oxidation. The molten metal is lifted in ladles a considerable height and poured in a thin stream through the air, back into the metal pots. This is repeated for a considerable time, the exposure of fresh surfaces of the metal to the oxidizing action of the air thus further purifying it.

The refined metal is finally cast into slabs or flattish ingots, which bear the brand or mark, indicating something of its origin and the standard of quality. These brands will be dealt with later, as the particular degree of purity usually obtainable from each grade of tin greatly influences its employment for special services, and thus also influences its market value. The utilization of the residues from the tin smelting is an important matter in modern economic working.

The collection of the arsenic as arsenious oxide has been mentioned. In many cases the oxides of sulphur also are converted into sulphuric acid. The tungsten, after it has been converted into alkaline tungstate, is dissolved out, and recrystallized and used by the makers of cotton fabrics, for rendering their materials non-inflammable. The greatly extended use of tungsten and tungsten oxide in manufacture renders this material a very valuable addition to the available supplies of compounds of this remarkable metal.

The residues left on the furnace during liquation and also the skimmings, drosses, and even the ashes from each refining operation, are treated in order to salve the valuable metal which they contain.

In this branch of the industry the greatest caution has to be observed. Residues demand as much care and attention as regards treatment as ores. They are usually included in suitable proportion in the charge of blast furnaces where the contained tin is to a large extent dissolved or "taken up" by lead, the resulting tin-lead alloy being subsequently refined by liquation, poling, and skimming.

In some large works lead-tin alloys are roasted very thoroughly in large reverberatory furnaces or softening pans, oxide of tin being produced together with fairly definite proportions of lead oxide and a small proportion of antimony oxide. This product is called "pan scum." Much experience is required to obtain the correct composition and character. The subsequent reduction of the selected pan scum produces alloys of a definite composition and standard purity which have a large industrial application.

The treatment of alloys of the character indicated for the separation of the tin and antimony has received much specialized attention from metallurgists in recent years.

Mr. H. Harris has patented a process by which he passes alloys of lead, tin and antimony in a finely-divided stream, through a fused bath of alkaline salts contained in a specially designed vessel. The antimony is converted into sodium antimonate, the tin into calcium stannate, and the lead freed from its previously associated metals and, being itself unattacked, is left in a highly pure and soft condition.

The tin is recovered from the calcium stannate, and

the antimony from the sodium antimonate by appropriate wet and dry operations.

The recovery of tin from the residual oxidized products is an essential part of the whole industry. The high cost of tin, and the expense of its extraction from the ore, are such that if only small losses of metal occur the whole operation becomes unprofitable. On the other hand, the employment in important industries of alloys which have been imperfectly refined, merely on the basis of low price, is extremely ill-advised, and the danger cannot be overestimated.

The accompanying table shows the character and amount of foreign substances or impurities in the grades or brands of tin which are recognized on the London Metal Exchange—

Antimony. Bismuth, Sulphur, Silver. Iron. Ľ'n. 99 939 Trace Trace 016 .004 Straits Penang 013 Nil 028 Nıl Straits Singa-99 870 -008 045 034 003 .003 006 005 pore 052 Mount Bischoft 99 9 Trace Trace .050 .01 006 01 .008 .005 022 Pyrmount 99.938 -017-019 Trace Nıl Trace Nıl .004 .007 99.950 Nıl -018 Trace Banca Trace Nıl ·045 Nil Billiton 99.960 .006 Nil Nil Nil .023 Nil Nil Nıl English Refined 99-860 .015 .040 .047 .006 -004 .005 .003 Nil Lamb and Flag 99-300 99.300 Chinese No. 1

APPROXIMATE TIN ANALYSES

The high standard of purity of metallic tin, now guaranteed by the metal exchange, and the accurate classification of the various brands, are features of the trade in our own country. As evidence the above table, issued by Messrs. William Jacks & Co. of Winchester House, Old Broad Street, London, is self explanatory.

The production of metallic tin of the highest degree of purity has been for a long time recognized as a most desirable object. It is a matter for congratulation that, after prolonged research and experiment, Messrs. Capper, Pass & Sons, of Bristol, have succeeded in producing a metal of extraordinary purity. It is called "Chempur" brand.

This variety of tin is extremely soft, having a Brinell figure of 3·23: a sample of Straits tin gave 8·0. It is very malleable. Tensile test pieces are found to draw off under load to a fine point at the fracture, thus giving an extraordinary "reduction of area"; tin of this degree of purity is very weak, under tensile stresses, only 0·88 ton to the square inch being required to break it, with the abnormal elongation of 86·5 per cent in 2 in. The resistance to corrosion and tarnish is well above the normal. Analyses of this metal are very interesting, thus—

	By Capper, Pass & Sons.	By Messrs. D. C. Griffiths & Co.
Copper	0.0005 %	0.0004 %
Lead	0.0030 %	0.0020 %
Bismuth	0.0005 %	0.0007 %
Antimony	0.0055 %	0.0050 %
Arsenic	Nil	Nil
Iron .	0.0020 %	0.0020 %
Zinc .	Nil	Nil
Manganese.	Nil	Nıl
Silver and gold	Nil	Nil
Sulphur .	Nil	0.001 %

It will be readily seen that manufacturers requiring tin of exceptional purity may rely upon the provision of the metal market to furnish supplies of grades to suit the purpose in hand. This feature is another example of the value of the co-operation of the smelters and refiners on the one hand and the merchants and their customers on the other, together with the scientific metallurgists and chemists, who have not only devised the methods of selection and refinement of the ores and products, but also standardized the analytical processes, in order to furnish figures which are as accurate as is humanly possible, and thus to guarantee a metal with confidence.

The methods of analysis are so extremely technical that they appear to be unsuitable for a small work of this nature. Generally the processes are based upon the principles which are described in the standard works of reference on metallurgical analysis, but it is usually found necessary, in the laboratories in which this highly specialized work is carried out, to modify the methods in various details to provide for the interfering action of impurities or special constituents.

Tin is a white metal, having a slightly yellowish tinge when compared with the pure whiteness of silver. It is bright and lustrous. Its melting point is 232° C. = 450° F. approx. It boils and volatilizes at a white heat (at between 1500° C. and 1600° C.). Its specific gravity is nearly 7.3. Its hardness lies between lead and gold.

Its structure is strongly marked crystalline, and, when a stick of the metal is bent backwards and forwards, it emits a crackling sound, which is described as the "cry of tin." This was at one time regarded as a test of the purity of the metal, but it is by no means so, as high grade solder gives a modified cry, and the absence of hard crystalline metals like antimony is not so markedly indicated. The cry is attributed to the grinding together of the crystals, and it naturally diminishes after repeated bending.

The pure metal, and also some rich tin alloys, are malleable, and can be hammered or rolled into very thin foil. It is ductile at about the temperature of boiling water 100° C., and can be drawn into thin wire.

At a little below its melting point it is capable of being crushed in a mortar to a powder. A rather remarkable feature is that at very low temperatures, as in the Arctic regions, tin disintegrates and falls to pieces, a fact which has to be remembered in connection with the employment of tin in the unalloyed condition either in abnormally cold climates or in refrigerating chambers or similar situations.

The crystalline condition of tin is interesting in other respects. Between the temperatures of 20° C. and 170° C. the stable form of the crystal is tetragonal, but above 170° C. the condition is rhombic.

Fine specimens of tin crystals can be obtained by various means. None of these is of commercial value, but they are excellent illustrations of the phenomenon of crystal formation.

If metallic zinc be immersed in a solution of tin chloride, fine crystalline dendrites of tin are deposited, which clinging to the framework of zinc form what is known as the "tin-tree." Another method is to melt the metal, allow it partly to solidify around the interior of the ladle or crucible, pierce the top crust with two holes, and empty the still fluid metal from the interior. Crystals of the metal are found to be lining the vessel; this requires some practice and skill to avoid disappointment.

A solution of tin-chloride slowly decomposed by a weak current deposits crystals. Zinc dust suspended in water added slowly to tin chloride solution also deposits crystals of metallic tin.

Tin being not readily affected by either dry or moist air at the ordinary temperature, this valuable property contributes to its serviceableness in the use of tin plate of all classes. When it is melted it gradually oxidizes, becoming at first grey through the formation of a mixture of finely divided tin and stannous oxide, the lower oxide of tin. This mixture gradually becomes completely oxidized, and is eventually converted to the white stannic oxide. Tin is slowly dissolved in hydrochloric acid, is soluble in hot sulphuric acid, in aqua regia, and when acted upon by nitric acid is converted into metastannic acid. This is an oxidization product, and consists of stannic oxide with the elements of water combined.

The commercial, domestic, and constructional uses of tin, which are legion, will be treated in separate chapters. They may be conveniently summarized into three groups—

- 1. The coating of iron, steel, and copper, for the preparation of tin sheets and the lining of vessels.
- 2. The preparation of alloys of very important character for engineering and manufacturing use, and the employment of the metal as pure tin in special and limited cases.
- 3. The use of tin compounds in more purely chemical and manufacturing processes, and to a small extent in medical work.

#### CHAPTER II

#### ALLOYS

The history of tin in its application to the useful arts throughout the ages proves that it has been notable for its profound effect upon the physical properties of other metals, and that this modifying influence on certain metals, such as copper and lead, has constituted one of the most useful if not the most useful of all the properties possessed by the metal.

This fact gives rise to a very common question from the casual observer, as to the nature of these alliances of the metals, or alloys, as they are termed. The metallurgist is frequently asked, "Is an alloy a simple mechanical mixture of metals or is it a compound of a chemical nature?" If it were possible to give a simple, definite and concise answer to this question, metallurgy would be a much simpler subject to study and investigate than it is. Possibly it would at the same time lose much of its interest.

Until the present generation, metallurgists have been generally content to add one metal to another, alloy them by melting, working, of course, on some systematic lines, based upon their own past experience and that of others; taking advantage of the known changes and modifications of properties, such as increased strength and hardness, which the metals undergo, through the mixing of these metals and their association with each other in the resulting alloy.

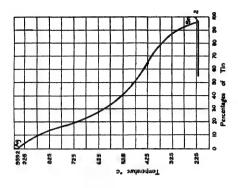
But it would have been at all times most unsafe to tell the inquirer that the alloy of, let us say, tin and lead or tin and copper is either a mere mechanical mixture of the two constituents, brought together by melting at an appropriately high temperature, or a definite chemical compound, as understood by the student of pure chemistry, or a simple solution of one metal in the other.

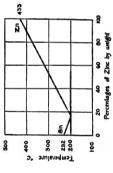
The last alternative is probably more nearly correct, but it is inadequate; the answer must include also a consideration of mechanical mixtures and of definite compounds.

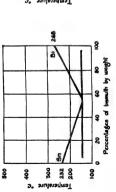
The metals in their molten or fluid condition have varying powers of solution in relation to one another. just as the common fluids of everyday life, such as water. alcohol, oil, petrol, etc., act as solvents upon other bodies or upon each other. But, as the metals (with the exception of mercury) are all solids at the ordinary temperature, the alloy or the products of attempts to obtain solutions of the metals in each other whilst in the molten condition, frequently consist of a very intimate mixture of crystals, which have separated in a solid state during the gradual process of solidification. These crystals are not all alike in composition, but comprise solid solutions of the constituent metals, compounds of those metals having a definite chemical formula, and also crystals of pure metal in excess of that which can enter into more intimate relationship with its fellows, or remain in that intimacy at the temperature of freezing or solidification.

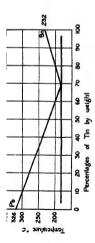
The portion of an alloy which remains fluid longest during the process of solidification is called the eutectic. It has therefore the lowest freezing point and the lowest melting point.

Close study of the phenomenon of cooling of alloys, using an electrical recording pyrometer to note and record the temperature at frequent intervals, discloses the fact that, as the process goes on, and various constituents crystallize out, breaks in the diagrammatic









3--(1463в)

COOLING CURVES OF TIN ALLOYS

Fig. 3

curve are noticed at the points when decided changes from the fluid to the solid condition are observed.

It is a notable fact that, when very pure metals are slowly cooled from the molten state, it is possible for the mass to be cooled below the ordinary freezing point before solidification begins; but, when the change does take place, the temperature rises to the normal freezing point. This is clearly marked in the cooling curve record of pure tin, when the experiment is conducted with great care. This is called super-cooling or "surfusion." A matter of considerable importance in considering the cooling of allovs from the fluid stateand this is true of tin alloys—is that, as the temperature falls, the solutions of metals change, until the composition of the two or more solutions is constant for a particular temperature These solutions, which can conceivably be separated by physical means, are called "phases," and are said to be in "equilibrium."

The alloys of tin are very numerous, and have been the subject of much investigation, for purely scientific purposes, in addition to their application for manufacturing uses.

Tin. Lead. The freezing curve of this series of alloys, strictly the ordinary solders, is given. The eutectic consists of about 63 per cent of tin and 37 per cent of lead, and melts at 180° C. This is the composition of blowpipe solder, its low melting point being a specially useful feature.

Tin. Silver. This series has led to some controversy as to whether a large number of definite compounds of silver and tin are formed, or a compound which is isomorphous (similar in form) to silver. The freezing point of this series is given.

Bismuth-tin. The curve of this combination shows that the eutectic is at 143° C., and consists of bismuth

55 per cent, tin 45 per cent. Tin also forms alloys of great scientific interest, with gold, sodium, nickel, magnesium, zinc. The last named is growing in commercial importance on account of its influence in the modern practice of die-casting.

The alloy series of tin and copper are all important, both from the scientific and the practical manufacturing standpoint, but they are rather complex. They, however, serve to illustrate the type of work now undertaken in connection with alloys of universal application, and also to show how wonderfully accurate was the earliest work, in almost prehistoric days, when it is considered how wonderfully similar is some of the earliest known bronze to our own gun-metal.

The series of crystals which form during the cooling of the copper tin alloys contains many members. As is usual, they are distinguished by letters,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\eta$ , H and Sn, also  $\varepsilon$ —

- a Contain 0 to 9 per cent of tin, they are solid solutions of copper and tin.
- $\beta$  Also solid solutions, with 22.5 to 27 per cent of tin.
- γ Also solid solutions which crystallize in a different system from the preceding members, composition 28 to 57 per cent of tin.
- δ This constituent does not separate on cooling directly, but is produced by an interruption between  $\beta$  and  $\gamma$ . It has a remarkably fine crystalline structure, and is probably a compound  $Cu_2Sn$ .
- η A series of fine crystalline lamellae, it is found to correspond to the compound Cu<sub>3</sub>Sn.
- H Approximately corresponding to CuSn, sometimes holding some Cu<sub>2</sub>Sn in solution.
- Sn Is, of course, pure tin.

E This is a more recently isolated constituent found in rich tin alloys.

The series of alloys in which tin is a very important constituent, just mentioned, are all binary alloys, that is, containing tin and one other metal in each alloy. Many of the alloys in which tin plays a vital part are ternary, 3 metal alloys, or quaternary, 4 metal alloys. The study of their constitution is infinitely more complex, and must provide work for generations of metallurgical investigators in the years to come.

The most recent investigation into the nature and constitution of the metals and their alloys is by X-ray analysis.

This has furnished the investigator with a further means of accounting for much of the observed behaviour of the metals, and has permitted him to visualize to a remarkable extent the structure of the crystal, and the arrangement of the atoms in building it up.

Some metals and alloys are found to have their constituent atoms arranged as if upon a cubic-formed lattice with an atom at each corner and another in the centre of the cube, another form of arrangement having an atom at the centre of each face of the cube. Other geometrical arrangements are known, such as a hexagonal prism.

Tin has not so far yielded its secrets in this direction very completely, and the arrangement of its lattice formation is not yet agreed upon.

We are yet hardly upon the threshold of this branch of investigation. It is already yielding most wonderful results, and must soon have a deep impression on the useful information at the service of mankind. What its future is can only be conjectured.

## CHAPTER III

## TIN-COPPER ALLOYS IN COMMERCE

PROBABLY the first serious application of the metal tin in the industries was its employment in the manufacture of alloys.

Copper appears to have been the first of the metals of the truly useful character to be known to man. After the gradual passing of what is generally known as the Stone Age, implements of copper came into use; or perhaps it would be more correct to put this statement in the reverse order—when copper came into use as the result of experiments by the early metallurgists, the use of stone implements was gradually superseded and discontinued. But copper was too soft for continual use, the edges of knives, axes, swords, etc., became rapidly blunted, and some means of hardening were required. Undoubtedly this was at first effected by hammering the metal, until by the effect of what is now called cold working a considerable degree of hardness was attained. This was not wholly satisfactory, as brittleness and cracking resulted. It is rather fascinating to imagine the anxious care of the early workers in their researches for some substance which. added to this useful metal, copper, would harden it and make it more durable. It is not improbable that at first metallic tin was not added, but that oxidized tin ores, together with some carbon or other reducing agent, constituted the physic which was added to the molten copper; or may be the metallurgist or alchemist had already succeeded in isolating the metallic tin, separating

it from the earthy impurities in the form of oxide, and then reducing it by carbon in some form.

Whichever was the actual method used, without doubt not only the public but the researchers themselves were greatly surprised by the wonderful results which were obtained by the alloying of the metals tin and It was found that tin had the power of hardening copper in a most remarkable manner, and it has not even to this day ceased to be a matter of wonder. For. if it be considered that when two metals, both of them tough—one red-copper, and another white-tin—are alloyed by melting them together in the proportions of two parts of the red constituent—copper, and one part of the white constituent—tin, the resulting alloy is a purer white than the white constituent, which constitutes only one-third of the alloy, and further, although both metals as stated before are individually tough, the alloy is as brittle as glass. Perhaps the ancients did not go so far as to obtain this result in their early experiments, but it would appear that they did so, for the influence of the tin was attributed to that of the Devil, and the subject of our study was named metallorum diabolus, or, roughly speaking, the metal of the devil. From this it will be seen that it was discovered that tin not only hardened copper, but whitened it in a most striking way.

This information must have been possessed at very early times by the learned men of some nations, for a rod of alloy was found by Dr. Flinders Petrie at Meydum, and is estimated to belong to a period of about 3500 B.C. This alloy on analysis was found to contain 89.8 per cent of copper and 9.1 per cent of tin, the remainder being probably oxide and impurities. This is indeed striking, and appears to have been the result of prolonged experiments and researches, for it should be noted that its

composition is remarkably close to that of modern alloys of that class. Gun metal, or the metal from which ordnance was made up to the time of iron and steel guns, and used in European countries until after the middle of the nineteenth century, consisted of 90½ per cent copper and 9½ per cent tin, and it will be seen a little later that other important alloys are based upon this one, or virtually are mere improvements of the metallurgical discovery of considerably more than five thousand years ago.

These alloys of copper and tin have been known as bronzes.

The earliest bronzes appear to have been of almost pure copper and tin, whilst those of the Roman period contained some lead. Whether lead was added with the definite object of slightly softening the alloy, or to make it somewhat more plastic under pressure cannot be determined.

The oldest metallic relic which can be dated with reasonable certainty is said to be a sceptre of Pepi I (6th dynasty). It is of almost pure copper. Bronzes have been found dating from very early times in Egypt. In Greece, Homeric period (900 B.C.), bronzes were rare, and the Greek and Trojan heroes (1194-1184 B.C.) appear to have used copper for their armour, swords, knives, and spear heads.

There seems to be no doubt that there was much overlapping of those periods which are spoken of as the Bronze Age and the Iron Age. Evidently the Iron Age, or the introduction of iron implements, took a long time to displace the Bronze Age, and did so probably as it was found that those nations which were armed with iron weapons gradually overcame those provided only with those of bronze, and this was true also in the arts of peace as in war. Iron implements and tools gradually

displaced those of bronze. But it must be remembered that the latter are much more enduring in their resistance to corrosion and the effects of time. The iron relics have gradually rusted and almost disappeared, whilst the bronze ones are in fairly good condition.

In Egypt, Assyria, and Babylonia, instruments of bronze have also been found, together with those of iron; whilst in Ireland, India, Cyprus, and other countries weapons of almost pure copper, and similar in form to those of stone, have been found.

The presence of zinc in bronzes was, in the early times, almost certainly accidental, due to the introduction of zinc ore in the furnace charge, or to impure ores of tin being employed.

The following table has been copied from Mr. Edward F. Law's excellent treatise on alloys. It completely confirms the early systematic use of tin for the hardening of copper, and the formation of excellent bronzes of varying composition.

	Copper.	Tın.	Lead.	Iron.
Celtic vessels	88.0	12.0	_	
Bronze nails	95.1	4.9		_
Bronze (Troy, 1200 B.C.)	90.7	8.6		
Bronze ,, ,,	93.8	5.7		
Roman sword blade .	91.4	8.4		
Coin of Ptolemy IX .	84.2	15.6		
Athenian coin	89.4	9.9		
Coin of Alexander the				
Great	86.7	13.2		
Axe-head	88.0	11.2	0.8	
Attic coin	88.5	10.0	1.1	
Coin of Julius Cæsar .	79-1	8.0	12.8	
Roman As. (500 B.C.) .	69.7	7.2	21.8	0.5
Sword blade	89.5	10.0		0.4

In modern times great attention has been given to the character and constitution of bronzes. In 1879 the committee on alloys appointed by the United States Board published a table in which the results of their own researches and those of previous workers were collected. These were concerned chiefly with the physical and mechanical properties of the various admixtures of copper and tin, and showed much of those features commonly spoken of as the useful properties for mechanical constructive purposes.

These tabulated results of the tensile strength, hardness, ductility, and other properties were most useful, and went to prove that the useful construction alloys are limited to two classes—

- 1. Gun metal with 8 to 14 per cent of tin.
- 2. Bell metal containing 15 to 25 per cent of tin.

As before stated, gun metal, as used for the manufacture of guns or ordnance, consisted of about 90 per cent of copper and 10 per cent of tin, or originally 90.5 per cent copper and 9.5 per cent tin.

Although this alloy has not been used in the actual construction of the guns proper for many years in this or other up-to-date countries, gun metal is very largely employed for fittings on gun mountings and ships fittings. In fact, there is no better known alloy in the whole of modern engineering and foundry practice than that known as Admiralty gun metal, which consists of copper 88 per cent, tin 10 per cent, and zinc 2 per cent. It would be impossible to give the number of variations of this alloy, but it is safe to state that the Admiralty alloy is accepted throughout the world as the standard of its class. Lead is added sometimes to soften, or to make more plastic, although lead is not dissolved to any considerable extent in the other constituent metals of the alloy, but is more or less evenly distributed in fine particles throughout the structure. Zinc is added both to harden and to strengthen; it

also acts to a limited extent as a dioxidizer, but acts in this capacity only towards the copper.

The present-day purposes to which the family of alloys generally known as gun metal is put are very various. The colour is deeper and more attractive generally than brass in the polished condition; the alloy is generally less easily corroded. The gradual discoloration which these metals take up when subjected to normal exposure to weather is termed the patina, and is a pleasing and very valued feature, in many instances. The alloys of this series are reasonably easy to cast, they are adaptable to many of the fittings such as taps, water cocks, and the many fittings with which everyone, however little interested in engineering and metallurgical manufactures as such, must be familiar.

The gun metal family, as has been shown, is one of the most enduring of man's manufactures. It is therefore of especial value in the production of statuary.

It is the modest but somewhat unsatisfactory fashion in our own country to decry our own productions, particularly those of an artistic character, and this is specially marked in the case of our statues; undoubtedly we deserve the criticism in many cases, and, whilst most of the reproach is directed to the design and artistic side of the production, the metallurgical aspect does not escape entirely. It is pointed out that our bronzes of all kinds are corroded, eaten away, decayed, and all sorts of things, and the delightful patina of notable statues on the Continent is much better.

There is some basis for these strictures, but the case is not so bad as it is made out. The atmosphere in London and many provincial cities is exceptionally trying, being due not only to climatic conditions, but more especially to the products of combustion of the coal fires, and the fumes from many factory chimneys; gases are discharged into the air of such a corrosive character that it is not surprising that bronzes, however well made, fail to withstand their attacks. The deposit of soot from the smoke-laden fogs and the common custom of fuel consumption in our towns is also responsible for much of this trouble, for galvanic action between the carbon and the metals, under the influence of moisture and acidulous gases, plays havoc with the surface of metallic works of art.

It has also been the subject of some reproach, whether deserved or not, formerly, that our statuary founders did not trouble enough about the composition of the alloys used, that true bronzes were often contaminated with much zinc due to the use of brass scrap, to make up their furnace charges, and perhaps to cheapen the alloy supplied.

The analysis of many of the famous statues on the Continent was made public, this course naturally providing a very certain safeguard against dishonest craftsmanship in metal-mixing. But the published figures give rise to much doubt whether these celebrated statues would have fared any better than our own if they had been subjected to the severe atmospheric trials of our great towns. Undoubtedly the presence of such large quantities of zinc would be looked upon as thoroughly bad and probably dishonest if found in work of English founders. The list on page 28 is taken from Mr. E. F. Law's Alloys.

It is considered that the addition of zinc makes the molten alloy more fluid. This is probably due to the deoxidation of the copper, but in any case it is reputed to facilitate the casting operation; but there seems to be little doubt that, when subjected to the corrosive action of the air and its impurities of an English town,

alloys containing zinc in any serious quantities take up a much less smooth and satisfactory patina, and are apt to become pitted or suffer local corrosion.

It has been stated that the patina on the backs of the Landseer lions in Trafalgar Square is very fine indeed.

	Copper	Tin.	Zinc.	Lead.	Iron.	Nickel.
Column Vendôme,						İ
Paris	89-20	10.20	0.50	0.10		_
Column of July,						
Paris	91.40	1.60	5.60	1.40		-
Henry IV, Paris .	89.62	5.70	4.20	0.48	_	_
Louis IV, equestrian						
statue, Paris, 1699	91.40	1.70	5.53	1.37		l —
The Shepherd, Pots-						
dam Palace .	88.68	9.20	1.28	0.77		—
Bacchus, Potsdam						
Palace	89.34	7.50	1.63	1.21	0.18	_
Germanicus, Pots-						
dam Palace, 1820	89.78	6.16	2.34	1.33		0.27
Mars and Venus,						
Munich, 1585 .	94.12	4.77	0.30	0.67		0.48
Bavaria, Munich .	91.55	1.70	5.50	1.30		-
Grosser Kurfurst,						ł
Berlin, 1703 .	89.09	5.82	1.64	2.62	0.13	_
Frederich the Great,						
Berlin	88.30	1.40	9.50	0.70	_	_
Melanchthon, Wit-						
tenberg	89.55	2.99	7.46	_		-

The late Sir William Roberts-Austen attributed this to equestrian exercises of the London street urchin, who, by taking frequent rides upon the lions, polished the successive layers of tarnish with the seat of his trousers, thus preventing thick deposits, and rapid or local corrosion.

The presence of a little lead is reputed to improve the bronze in respect to easy running and satisfactory founding, and also to improve the tone of the patina. It will be some satisfaction to us to know that the composition of the bronzes employed in the statues erected during the last ten years to the honour of several of our distinguished soldiers is beyond reproach. The metal used was that of a number of old guns in the possession of the Government. It was found that only British obsolete guns were entirely suitable. A number of trophy guns, captured or acquired from foreign countries, were analysed and discarded; only the British were of consistently good gun metal, zinc was absent or existed in slight traces only, and very small proportions of lead were found; a large number were used, and the analysis of every one was carried out with great care.

Here is a striking example of the different behaviour of two alloys, under exactly similar atmospheric conditions, after many years' exposure. The Bhurtpoor gun, one of the most beautiful bronze cannons in the world, has been for generations mounted upon a fine bronze carriage on the Artillery Parade, Woolwich.

The gun, which weighs about 16 tons, had evidently before capture been repaired after bursting. The rear portion of the gun (it cannot be described as the breech end, as the gun is a muzzle-loader) has had a new end cast over the old one; the newer portion is a high zinc alloy or brass, the original body of the gun is of gun metal. Whether the later generations of Hindoo founders knew or not cannot be said, but the artistic effect after the passage of many years is very marked and is worth careful attention. As in many Oriental castings, this gun metal is reputed to contain gold. Careful analyses have, however, failed to find evidence of the precious metal.

Coinage Bronze. The bronze or so-called copper coins used in our own country have consisted of copper

95 per cent, tin 4 per cent, and zinc 1 per cent. It was introduced here in 1861, but France was using the same alloy in 1852. Many countries have gradually replaced the bronze coinage wholly or partly by so-called nickel coinage, really a copper-nickel alloy. It was very strongly advocated that such a step should be taken in the United Kingdom, especially just after the conclusion of the War, but this did not take place, and the copper-tin-zinc alloy is still used. It is excellent in many respects, it is sufficiently malleable and ductile to take a sharp impression of the die, it withstands wear, largely by the rubbing of coins together either in handling, packing, or in the pocket, and is strong and durable. The natural patina which gradually develops upon the coins in general use is such a familiar feature that it does not excite the interest or attention which it deserves. Medals in bronze are struck from allovs very similar to coinage bronze as a rule. The colouring of these is a matter of great importance. Generally the medals are immersed in baths of mixed alkaline sulphides, and washed and dried with great care. The bronze victory medal which was issued with the silver service medal was the object of the greatest care, in order to obtain not only a perfect definition, but absolute uniformity in colour.

The Victoria Cross is also a bronze of the copper-tin series. Originally these coveted decorations were struck from gun metal, taken from trophies from the wars with Russia, and possibly earlier French actions. During the Great War further material was required, and it was decided that metal should be obtained from guns other than those of our allies. The cascable or round end of several Chinese trophy guns was therefore cut off and converted into strip for striking Victoria Crosses. The memorial plaques which were sent by His Majesty

the King to the next of kin of all officers and men alike, in all the Services, who gave their lives in the Great War, are very fine examples of bronze castings in sand moulds. It is probable that nothing of the sort has ever been done of such quality and large numbers before.

Bell metal consists of copper and tin. Other metals should, as a rule, be entirely absent, or only occur in slight traces.

The proportion of tin varies from 15 to 25 per cent, usually, so that in a general way it is customary to regard this alloy as consisting on the average of 80 per cent copper and 20 per cent tin.

From what has been already stated it will be perceived that bell metal is a hard and somewhat brittle alloy. The tone of the bell is somewhat modified by alteration in composition, but the purity of tone is dependent upon the design and the accuracy of founding, rather than composition.

The following figures have been collected by Mr. Law-

	Copper	Tın	Zinc.	Lead	Antı- mony.
Large bells .	76	24	_		
House bells .	78	22			_
	80	20	-		_
Musical bells .	84	16			
Clock bells .	75	25		_	_
Old bell at Rouen	71	26	1.8	1.2	_
Small bells .	40	60		_	
,, ,, .	_	87.5			12.5

As regards English bells the earliest existing example to which a date can be affixed is to be found in the village of Claughton, near Lancaster. It is slightly over 16 in. in height, 21 in. in diameter at the lip, and bears the date 1296. From this time bells with

inscriptions and dates are to be found, and the history of bell founding in this country can be traced. The earliest instructions for bell founding occur in a treatise by Walter of Odyngton, a monk of Evesham, in the time of Henry III, who describes the method of founding and also the method of determining the relative sizes of the bells necessary to produce the required notes.

Many of the well-known large bells have been recast from older bells. Thus "Great Dunstan" of Canterbury, weighing 3½ tons, was recast in 1762 from an old bell, originally the gift of Prior Molass in 1430. "Bell Harry" was recast in 1635 from an old bell said to have been presented by Henry VIII. Another famous bell, "Great Tom" of Oxford, has had a very chequered career. Originally removed from Oseney Abbey to Oxford on the suppression of the monasteries, it was recast in 1612, again in 1654, and later in 1680. Three unsuccessful attempts were made to recast it, the mould bursting in the third attempt, probably through improper or imperfect drying. A further attempt was made in 1741, this time with success.

Of modern bells "Peter" of York is one of the largest. It was cast by Charles and George Mears at the White-chapel foundry in 1845. It weighs about  $12\frac{1}{2}$  tons, and is 7 ft. 4 in. in diameter.

The original "Big Ben" of Westminster was cast by Messrs. Warner & Son in 1856, and weighed 14 tons, its diameter being 9 ft. It soon became cracked; it was recast by Mears at Whitechapel, this time slightly lighter, with a clapper only 6 cwt. instead of one ton, the original weight. "Great Paul" of St. Paul's Cathedral was cast at the Loughborough Foundry in 1881. It weighs 16 tons 14 cwt. 75 lb., its diameter is 114\frac{3}{4} in.

Bell metal is susceptible to heat treatment. When

heated to redness and chilled, it is more malleable and of a more yellow colour than when slowly cooled.

This heat treatment of bronzes introduces a very difficult and complex branch of the study of alloys. Modern metallurgists have given much close study to this feature. It is found that the alloys of tin and copper are by no means simple in their constitution. A solid solution of tin in copper is formed which contains varying proportions of a definite compound of the two metals having the composition Cu, Sn. This compound appears to form on the solidification of the alloy. The compound is white when viewed under the microscope, whilst the ground mass of copper-tin solid solution is yellow. This solution contains approximately 9 per cent of tin, and it may therefore be taken that roughly any tin content above that amount goes to form the hard white compound. This accounts for bell metal, which frequently contains over 20 per cent of tin, being almost white, at the fracture. As the white compound forms and separates at or near solidification, it is evident that this formation is hindered and the separation arrested or diminished by chilling a casting from a dull red heat.

The exact physical interactions are not as simple as is indicated, but take place in a series of stages. These functions have been studied and recorded by Charpy, then very thoroughly by Haycock and Neville, and later by Houghton. The researches did not appear to the craftsman to be particularly useful, and to have only an academic interest; but this has proved to be quite a mistake, for the added information was soon found to account for many features which were not understood, and has enabled technical processes to be systematized in the light of the newly acquired knowledge.

Phosphor Bronze. One of the principal developments of the bronzes or copper-tin alloys is phosphor bronze.

It is held by many that the birth of this alloy was the outcome of an attempt to deoxidize the metals in the crucible by the addition of an extremely oxidizable substance, phosphorus. The fact that it was found possible to prepare compounds of tin and copper respectively with phosphorus made the addition of the latter element a practicable operation in the foundry, whilst handling the molten metals, and it was at one time thought that any advantage gained in the way of better physical and mechanical properties in the resulting alloy was due to the deoxidation and cleaning of the metals in the crucible, and thus presenting the constituent metals to each other in a form which is favourable to the perfect solution and combination into and with each other. That this is in a measure perfectly true is granted, but a great deal more is evidently done, and moreover it is now thought that although copper is deprived of its oxygen impurity quite readily by phosphorus, tin is not by any means so amenable to treatment. It is therefore fairly clear that some other features are present in the newer alloy.

Phosphor-tin is a crystalline and very beautiful substance, containing varying proportions of phosphorus from 3 up to 10 per cent, the most usual proportion being approximately 5 per cent. The addition of the phosphorus is generally made by adding phosphortin or phosphor-copper to the crucible charge at or towards the end of the melting operation. The effect upon the molten metal is very marked, and the experienced operator can readily see if the addition has been made by the appearance of the surface of the molten metals. A glistening and rapidly moving film is seen to be spread over the surface, instead of the heavy, dull, oxidized character evident in the alloy which has not received the addition.

Phosphor bronze, therefore, may be looked upon as a greatly improved gun metal. It is stronger and harder. It resists corrosion to a marked degree. Its increased hardness is largely due to microscopic separation of copper-phosphorus and tin-phosphorus compounds embedded in the alloy. The addition of lead is found to be very beneficial to the metal for bearings. The alloy is slightly plastic, and the slightly mottled bearing surface produced is undoubtedly of great value. This probably also assists in the distribution of the lubricant.

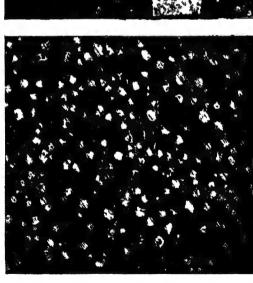
## CHAPTER IV

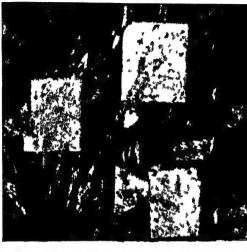
## THE WHITE METALS

THE family of white metals is a very large one. The preparation and trade in these alloys form a very important branch of metallurgical industry, but, although a great deal of investigatory work has been carried out in connection with it, the amount of attention it has received compared with the so-called yellow metals, or alloys of which copper is the chief constituent, is very small. Probably for this reason, the manufacture of these white alloys, chiefly composed of tin, antimony, and lead, with small proportions of copper, has been regarded as a business with many so-called trade secrets. There are certainly secrets, but the more important of these lie in the skill and experience of the workers These workers are of all grades, and comprise furnace men and metal mixers on the one hand and highly trained scientific metallurgists on the other, as well as a whole army of foundry men, moulders, rolling mill hands, platers, and also engineers and tool and die makers; each man plays his part and none is independent of the others.

For practical purposes alloys, which are generally described as white metals, may be classified as follows—

- 1. Anti-friction or bearing metals.
- 2. Printers' metals.
- 3. Pewters and Britannia metal.
- 4. Solders.
- 5. Special alloys used for castings for chemical works, building services, battery plates, bullets, collapsible tubes; foil for wrapping tobacco, chocolate, etc.





(b) No 1 Alloy senously overheated  $\times$  100 Fig. 4 (a) No 1 Alloy showing Copper-Tin constituent × 100

ANTI-FRICTION METALS, PHOTOMICROGRAPHS

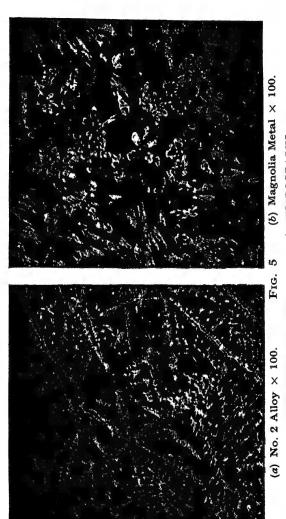
- 6. Die casting alloys.
- 7. Toy and mould metals.

Anti-friction Alloys. In the earlier days, the linings of bearings of running machinery were usually made of gun metal, and later of phosphor bronze. These alloys are still in use to a very large extent (they are described in their own family group), but in more recent times the yellow metal linings, or brasses, as they are frequently though incorrectly called, have been displaced by white metal. The highest grade white anti-friction alloys have as their chief constituent tin, and consequently are very expensive, but the proportion of tin is gradually diminished in the less costly alloys.

The description and report of tests of these alloys are abstracted from papers presented to the Institute of Metals and published in the Journal of the Institute, the more severely technical portions being omitted in this description, as they are regarded as too specialized to be of general interest.

The exact physical properties required in a lining for a bearing are not universally agreed upon. It is generally admitted that in the ideal journal the shaft never comes in contact with the bearing at all, the metallic surfaces being completely separated by a film of oil. If it were actually possible to attain this in common practice, the composition of the bearing metal would appear to have little importance. As the ideal conditions are not practicable, it becomes a matter of serious moment to provide a metal that will meet the mechanical conditions imposed, as well as present the kind of surface that will promote the spreading and maintenance of the oil film.

The engineer demands a certain balance of properties in a bearing. It must be sufficiently hard and strong to resist distortion under working loads and irregular



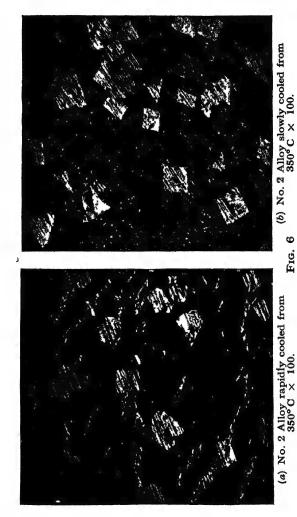
ANTI-FRICTION METALS, PHOTOMICROGRAPHS

stresses. It must present a fine surface, not liable to rapid abrasion, and on the other hand must possess a measure of plasticity which will permit it to accommodate itself to slight want of alignment of shafting, and it must be sufficiently tough to resist fracture under shock.

Experience has established the opinion that a homogeneous alloy is not suitable for a bearing, that neither a single metal nor an alloy which is a solid solution can be employed with success, but that either a metal consisting of a soft matrix with hard crystals embedded in it, or a hard metal interspersed with veins of a softer constituent has the necessary surface for a practical bearing alloy. There can be no doubt that the best service is obtained from an alloy which, though not homogeneous, has its undissolved constituents distributed in a regular and uniform manner. This mottled surface, in which the harder portions are in slight relief. provides a number of pools and canals, which serve to retain the oil film and, on account of their fine and even distribution, promote the spreading of the oil over the surface.

There is no doubt that the rotation of the shaft plays an important part in carrying the oil film, but it is abundantly proved by experience that the desired conditions are promoted and almost exclusively obtained, when metals of the character described are employed.

The engineer when making a choice of materials for any constructional work usually desires to visualize the properties of these materials in quantitative terms, and his thoughts naturally turn to tensile strength, hardness, and resistance to compressive stresses; for, even when the particular stresses to which he is about to subject his construction or mechanism are not strictly represented by simple tensile or compressive forces, he



ANTI-FRICTION METALS, PHOTOMICROGRAPHS

is able by experience to decide on the suitability of the material by the results of tests, expressed in terms of tensile strength, compressive strength, etc.

The following alloys are fairly representative types of bearing metal, in the composition of which tin plays a very important part; and, in order to make the story fairly complete, the results of tests are given, in addition to the composition.

The results are strictly comparable, as all were cast under the same conditions. The casting temperature in all cases was 350° C., the mould of cast-iron being heated in all cases to 100° C. The test pieces for tensile test were turned to a diameter of 0.564 in., and the acting portion was 2 in. long, this being according to the usual practice, and conforming to the specification of the British Engineering Standards Association.

The tests for hardness were made by the well-recognized Brinell method: a hard steel ball of standard diameter pressed upon the surface of the metal to be tested for a period of about 30 seconds; the diameter of the circular cavity is carefully measured under a microscope, the area of the concave surface computed, and a figure obtained which represents the amount of resistance to the stress, and capable of comparison with other results similarly obtained. The ball used was 10 mm. in diameter, and the load was 500 kilogrammes.

The compression tests were made by taking cylinders 0.564 in. in diameter (this diameter gives an area of just 0.25 sq. in.) and 0.5 high. The cylinders were squeezed vertically under a hydraulic testing press; the pressure was noted when the test piece was permanently shortened by 0.001 in. (one-thousandth part of an inch). The pressure was still maintained and the deformation noted as the test proceeded. The figures given are for the first observable deformation, and when

the cylinder had been crushed to one-half its original height.

This alloy is quite free from lead, and combines maximum toughness with strength. It was mostly favoured for the big-end bearings of aero engines, having gradually replaced somewhat harder but less tough alloys. It is probable that it is the best bearing metal produced for strenuous and critical services. Efforts have been made further to improve it by addition of other metals in small quantities. Some claims of success are put forward, but tests of a very elaborate and exhaustive character, by the author and his colleagues, entirely fail to support these claims. The test results are as under—

Tensile Test.		Brinell Hardness,	Compression Test.		
Tons to square inch.	Elongation per cent on 2 in.	No.	Tons to square inch.  Compressed Compressed to  0.001 in. half length.		
5.12	11.6	24.9	3.569 14.732		

The structure of this alloy is characteristic and interesting. Tin is capable of dissolving a considerable quantity of antimony when molten, and of retaining about 7 per cent in solution on solidification. If more than that amount is held whilst the metals are fluid, the excess of antimony (over 7 per cent) crystallizes out before solidification, and this can be seen in the form of cuboid crystals when an etched specimen is viewed under the microscope. In alloy No. 1 this cuboid structure is not in evidence, as the amount of antimony is only 3.5 per cent, and remains in solid solution. The copper, however, exhibits its well-known tendency to

form hard compounds with the tin, and partially separates on cooling, showing a lace or net work of fine needle-shaped crystals. These needles are very hard, and remain embedded in the tough and hardened tin-base matrix.

The photomicrograph (1) shows these crystals very clearly. The alloy was cooled rapidly, through the rapid conduction of the heat by the iron mould.

The tough matrix gives the alloy the power to resist shock and bending stresses, and also the destructive power of constant and rapid vibration; the evenly distributed hard crystals provide the mottled surface resisting abrasion, and the softer, tougher matrix, being to a microscopic extent rubbed away, combines to give the surface necessary to maintain the oil film and make the highest grade anti-friction material yet known.

This is also free from lead, it is harder and less tough than No. 1, and is more nearly the earlier conception of the ideal bearing metal. It is an excellent alloy, and possesses anti-friction properties quite equal to, if not in advance of, No. 1, but, in getting the extra hardness and resistance to abrasion and compression, some sacrifice of toughness has to be made, and in an aeroplane engine the breaking of a bearing is too great a source of danger to be permitted.

The structure of this alloy is also most interesting, and provides for the reader and student of metals an object lesson in the relations of the various constituents of an alloy, both striking and informative.

In the process of cooling, the molten metal first deposits rich copper-tin crystals, of needle shape, which

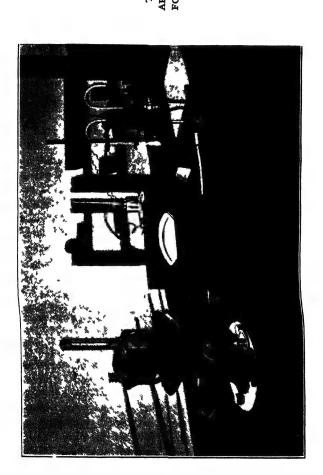


FIG. 7
TESTING
APPARATUS
FOR WHITE
METALS

form a fine lace-like structure throughout the mass, and at a little lower temperature cuboid crystals of antimonytin fall out. These are enmeshed in the already formed but still soft-solid copper-tin compound, and finally the matrix of tin base alloy containing both antimony and copper solidifies. We thus have two distinct compounds, both hard, embedded in the tougher but moderately hard matrix. The surface presented to the rotating shaft is almost ideal in this case.

It is the practice in many marine engineering works, as well as other establishments, to hammer-dress, as it is called, the bearing after casting; this is to hammer the metal to ensure soundness and superior density. It is feared, however, that the effect of this is to crush the crystal growths, and somewhat to diminish the natural interlocking. The old custom dies hard, as it is a survival of the well-known improvement due to working of many metals, but the bearing metals of this family are usually good tempered, and it is thought that the damage sustained due to moderate hammer-dressing is not great.

The test results of No. 2 alloy are as follows-

Tensile Test.		Brinell Hardness.	Compression Test. Tons to square inch.		
	Elongation per cent on 2 in.	No.		Compressed to half length.	
6.65	7-1	33.3	4.372	17.232	

The size and distribution of the crystals are greatly affected by the rapidity of the passage of the metal through the cooling stages. If it cools very quickly, the crystals are very small and evenly distributed; but, if the cooling be very slow, as when poured into a very hot casing, the crystals are very large. The two photomicrographs of this alloy shown in Figs. 4 and 5 were taken from specimens cast from the same ladle, so that the composition is identical; the magnification



FIG 8
TESTING
APPARATUS
FOR WHITE
METALS

is the same, but the specimen shown in Fig. 6 (a) was cooled very quickly, whilst in that illustrated in Fig. 6 (b) the cooling process was prolonged purposely for over two hours.

The effect of a proportion of lead on the properties of these alloys is shown in No. 3.

The composition is-

In this case we obtain 5.6 tons to the square inch tensile strength, no elongation; that is, the alloy breaks without previous stretching, the hardness No. is 34, and the resistance to compression is very similar to the previous case. The test results do not, however, show everything, for it is found that this alloy is excellent in its resistance to shock.

The so-called Babbitt metals are legion; the name, like many other proprietary names, has been adopted to represent a class by makers all over the world.

The original patent Babbitt metal was a very high tin content alloy. It was prepared in a special manner, and it was probably this somewhat mysterious method of metal mixing which enabled it to be patented, as simple straightforward alloys are difficult to protect by patent.

A typical set of present day Babbitt metals is shown on page 49.

No. 8 is an alloy which is frequently called plastic metal. In some cases a little lead is added. It is used very extensively by millwrights and marine engineers for repair jobs, it is hard and durable, and it is self tinning. The name "Plastic" is given on account of

its behaviour during the process of solidification, and it is due entirely to its constitution.

The period of solidification, from the moment of the falling out of the copper-tin constituent to the final freezing of the last portion (termed the eutectic in these cases), is an extended one, and during this period the metal is in a plastic condition, consisting, as it does, of a mixture of crystals and liquid. It will "bind" in

	Tin.	Antı- mony.	Copper.	Lead.	
4.	80	11	3	6	Useful for heavy loads at high speeds Diesel engines, turbines, rolling mills, locomotives.
5.	60	10	1.5	28.5	For internal combustion en- gines, steam engines, dy- namos, locomotives
6.	40	10	1.5	48.5	A generally useful alloy for heavy pressure and medium speed, or medium pressure and high speed. Automobile engines, railway and tram- way bearings
7.	20	15	1.5	63.5	A useful metal for medium pressures and speed, or light pressure at high speed
8.	78	11	11	Nıl	pressure at high speed

much the same way as thawing snow, and for a similar reason. It is, therefore, capable of being spread and fashioned into the form required somewhat like the function of making a plumber's "wipe joint." Repairs of an extensive character have been effected with this metal at sea and on the field behind the battle lines, and the artificer who is working at a distance from his repair depôt or supply base is usually careful to have a small stock of it to hand.

The last alloy of this series to be mentioned is that 5—(1463a)

known as Magnolia metal. This is, however, a lead-base alloy, having antimony to harden and tin to harden, toughen and refine the product. It is deservedly a very good alloy, and it is a matter of some wonder that engineers do not somewhat modify the design of many bearings to enable it to be used even more extensively.

The composition is-

Lead 80 per cent Antimony 15 ,, ,, Tin 5 ,, ,,

Small traces of bismuth and of nickel have been added by experimental makers, but it is doubtful if any benefit is noticed due to the presence of the small quantities of these constituents, excepting that when experimental alloys are made a little more than usual care is exercised in the process.

The feature of the fractional solidification of these white alloys is recognized by all metallurgists and students, but not so in many cases by workmen and others engaged in their industrial application. For this reason the chief benefits which accrue to their correct. use are sometimes lost. This occurs in the following manner. The metal is melted in a ladle, little regard being paid to the temperature conditions. It is sometimes poured too hot, then it is allowed to cool and, toward the end of the operation, pouring is continued when a partial solidification has taken place in the ladle, the still fluid metal being poured off the semi-solid residue. These portions are not of the same composition, as will be understood from the foregoing account of the constitution. An examination of a pouring ladle after use frequently reveals a considerable residue of metal lining the vessel. On analysis this is shown to consist of the rich copper-antimony-tin compounds of higher

melting point, which, through their solidification, have remained behind, impoverishing the later pourings to a serious extent. Thus a series of bearings may be found to be of varying composition, even when poured from one-ladle contents, simply through inattention to temperature conditions. This has undoubtedly been the cause of many complaints of unequal wearing of bearings, some being hard and some soft, when cast from the same pot or ladle of metal. Fortunately skilled mechanics are now much more familiar with the control of temperature by pyrometers, and are careful to observe the changes and to avoid the pitfalls which are more or less common in the use of these excellent alloys.

# CHAPTER V

## PRINTERS' ALLOYS

THE craft of printing is dependent upon a series of white metal alloys of which the various classes of type are made, and in which tin takes a prominent and essential part.

For some hundreds of years it had been the practice of the printer to have supplies of type, each letter and character a single unit. These individual types were selected by a compositor and placed in position, together with specially cast pieces of metal and some wood blocks to form the spaces, into a frame called a chase, until the whole page was built up. It was then securely locked up, with wedges called quoins. This completed page of type when ready for printing is called the forme.

The alloy used for this type varies according to the size and character required, but usually consists of 5 to 20 per cent of tin, 25 to 30 per cent antimony, and the balance lead. Even larger amounts of tin were in the old times sometimes used, but consideration of cost has brought about a general effort to keep the content of tin as low as possible. The important part played by tin in the final product, that is, the actual printed page, renders this a matter of great moment. A little tin saved may lower the first cost of the alloy, but the loss of high finish and refinement of the print, as well as the great loss of efficiency in the production of type, greatly outweighs any apparent saving in the first cost.

The introduction of machines for casting and composing the type has been one of the great triumphs of engineering skill. The study of these machines, which play such an important part in the life of the present time, particularly in the rapid production of newspapers, is a most fascinating one. The response which the metallic alloys of tin, lead, and antimony yield to the great demand upon them is wonderful.

The machines chiefly used are the linotype, intertype, typograph, and linograph. These are in one class and are similar in general principle, differing only in the details of mechanism

The whole object of these machines is to cast a line of letters corresponding to an ordinary line of print, either for a newspaper or for a book page. The type faces are cast upon the edge of a slug or small plate. These slugs are simply packed together in correct order to form the column or page.

The operation of the linotype machine is typical, and is really beautiful in its mechanical ingenuity. The operator works at a keyboard similar to that of a type-writer, and is able to assemble in position by the action of an automatic selecting apparatus, a series of brass matrices, corresponding to the line of print to be produced; these matrices form the tront part of the mould, the remainder or mould proper is of steel in four parts, and corresponds to the body of the slug to be produced.

A simple movement of a lever actuates a pump, and molten metal is forced through a series of holes in the mouthpiece of the pot into the mould. The resulting casting or slug, having on one edge the line of type faces, is trimmed by sharp knives, ejected from the mould and placed into position in readiness for the forme. It has been found possible for one operator to produce upwards of 20,000 letters an hour. This should be regarded as a somewhat exceptional performance.

The metal used for this work is of much lower grade, and is softer than that used for type commonly set up



Used in preparation of Printing Alloys Fry's Metal Foundry BOTTOM POURING MELTING POT

by hand. It is composed of 2.5 to 3.0 tin, 10 per cent antimony, 87 to 87½ per cent of lead. Some printers desire a slightly harder alloy, and a corresponding increase in the antimony and sometimes of the tin also is made. These exceptional alloys require special care in their manipulation.

The metal is heated and maintained in a molten condition by gas burners or by electrical heating. Thermostats, either gas or electrical, are employed in many cases. The modern printer also controls the heating of his metals with an electrical pyrometer. The alloy used for the casting of these slugs solidifies at about 238° C. It has no prolonged period of solidification, and passes almost instantly from the fluid to the solid condition.

This is necessary, as the operations of casting, solidification, trimming, and ejection are so rapid in succession.

The requirements are an absolutely fluid and mobile metal; absence of contraction at the instant of solidification, thus ensuring a sharply defined casting; rapid solidification and little or no expansion or the ejection of the slug is hampered. The comparative softness and weakness of the metal is not a drawback, as the type members are mutually supporting one another in a sort of mass formation, and are thus enabled to resist the compressive and slight bending stresses encountered in service.

Purity of the constituent metals is most important. Traces of copper give rise to the formation of the hard copper-tin and copper-antimony constituents already described. These solidify at least 40° C. earlier than the rest of the alloy, and tend to clog up the mouthpiece. Zinc is fatal; it is not soluble in the alloy, but forms spongy, soft solid masses. Even very slight traces of

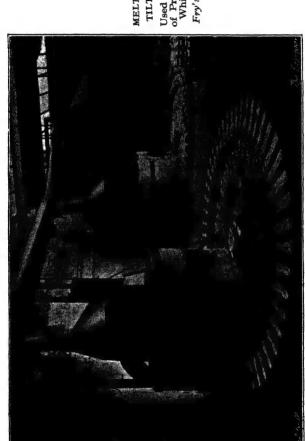


FIG. 10

MELTING POTS AND
TILTING FURNACE
Used for preparation
of Printing and other
White Metal Alloys
Fry's Metal Foundry

zinc spoil the fluidity of the metal. Nickel, iron, sulphides, and oxides are sure causes of trouble.

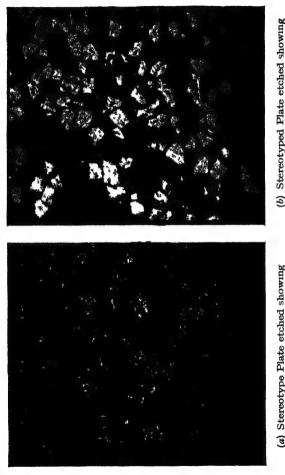
In some of the machines casting slugs, a slot is used instead of a series of holes, to enable the molten metal to pass to the mould. In these a slightly harder metal is capable of use.

The other important machine for typecasting and setting is the monotype. Both its own mechanism and its productions have reached the highest stage of perfection.

It consists of two separate members: first, the keyboard, by which the operator manipulating the keys causes the machine to punch holes in a long paper band, producing a roll or spool of paper somewhat like a pianola roll. This is transferred to the second mechanism, "the caster," and, as the spool rotates, the perforated paper is brought over a compressed air nozzle; the air impinging upon it passes through the holes and actuates the apparatus which brings an appropriate matrix into position. The instant this is presented to the end of the mould a pump forces a small quantity of molten metal into the mould and a single letter is cast. These letters are collected in proper order and placed into position automatically. As the name implies, the types cast are single and separate; they therefore require to be stiffer and harder than those cast into line slugs, not having the mass support of the latter. There are, however, compensating advantages. The small size favours very rapid solidification, more tin and antimony can be employed in the alloy without risk of dangerous segregation, and type of extremely fine face can thus be produced.

A good average alloy for monotype is tin 8 per cent, antimony 15 per cent, lead 77 per cent.

Sometimes harder alloys are demanded, with 10 per



(a) Stereotype Plate etched showing dots (180 imes 180 screen imes 100)

(b) Stereotyped Plate etched showing structure of metal as (a) in composition  $\times 100$ 

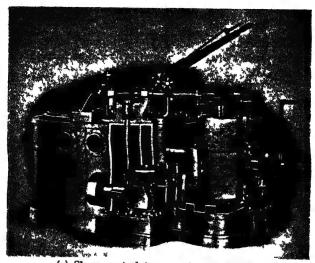
Fig

cent tin and up to 20 per cent of antimony. Great skill and experience are required by the operators to use these special alloys.

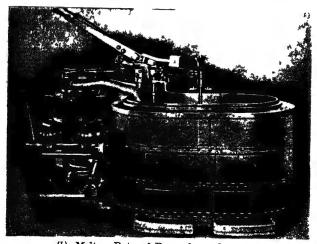
The exact function of the tin in these alloys has been the subject of much speculation and some controversy.

It reduces the melting point of the alloy, and makes the metal flow freely. It adds a degree of toughness to the hardened alloy of lead and antimony. It refines the structure, causing a formation of a fine, compact, crystalline growth, and the cast surface which is an allimportant matter in the face of the type is smooth, gives sharp definition, and a perfectly sound and unbroken surface. These features are of the greatest importance. A sharp, well-defined type face, smooth, without signs of frostiness, tough so that dots, hair lines, tails, and serrifs shall not break off, are all necessary for the production of good print. And every craftsman who is proud of his work insists upon these conditions. A further matter is of much commercial importance. The modern printer is a rather highly-paid worker, and his machines cost a large sum; any loss of time due to sticking of metal in moulds, nozzles, and mouthpieces or other troubles of a like character, are very expensive items, and the loss in money value soon makes the saving of the cost of a small percentage of tin a matter of regret.

Stereotyping. The operations of stereotyping are by no means so well known and understood as the subject deserves, considering that practically every individual in a modern civilized community reads and handles a newspaper every day, and one is thankful to know there are very few who do not use and appreciate books in a greater or less degree. Almost all newspapers and books are printed from stereotype plates, and, if an apology is needed for a short description of this section of the



(a) Shows cast plate in position in mould



(b) Melting Pot and Pump for molten metal
Fig. 12
TWO VIEWS OF AUTOPLATE MACHINE FOR CASTING
ROTARY PLATES FOR NEWSPAPERS

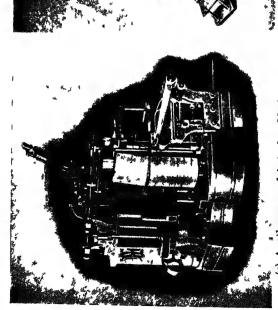
printing craft, the universal application of it to the service of mankind should constitute that apology.

When the type has been set up, either by the compositor by hand setting, or by the linotype or monotype machines, or others of their class, the columns of type, with illustrative matter, zinc plates or zincos, spacing material, etc., are securely locked up in a frame called a chase, and the whole page thus prepared is called a forme. It would be quite possible to print from this and, in fact, this is frequently done for small editions. Proof prints are taken, then the forme is placed upon a level table and a sheet of slightly moistened prepared papier-maché material, called flong, is impressed upon it, either by mangling or by beating by hand with a special brush. It is dried in position, and, the flong removed, it is found to have an accurate impress upon it of every type and illustration, true to the finest detail. It is now placed into a cast-iron box, and when properly fixed and adjusted forms one side of a mould, and is now called a matrix. The casting boxes are flat. rectangular fitments for casting flat plates, or half cylindrical when required for casting rotary plates. In the latter case the papier-maché matrix is bent to conform to the cylindrical curvature of the casting box. the whole is made warm, and molten stereotype metal is carefully and skilfully poured or pumped as in the modern machines, which are now so largely used.

The plate is taken out after casting, trimmed, examined, and if perfect, as it usually is, is ready for use in printing on either the flat bed machines or the wonderful rotary machines.

The most important machines are the Autoplate, the Junior Autoplate, and the Winkler casting machines.

The illustrations will render a too lengthy description unnecessary. In the first, the plate is cast in the







(b) Winkler Machine showing mould open . 13 with plate ready

horizontal position, and the metal entering the mould sweeps out the air, a supply of metal at the head giving not only fluid pressure, but a reserve for feeding the casting as it solidifies.

The trimming and boring of the plate are effected in rapid succession, and the finished plate is delivered at the end of the machine practically ready for the press.

The Junior Autoplate is cast vertically with a head of metal, commonly called the tail, above, providing the metal for feeding the casting and giving the necessary pressure.

The plates are cooled rapidly by passing a circuit of water through the parts of the mould, the walls and mandrils being made hollow for that purpose. The water cooling is a most important matter, any irregularity or mishap in this produces "sinks" and other defects. It is generally desired that the cooling should proceed from the back to the front of the plate, and from the portion furthest from the head towards the head. Pouring temperatures vary from 550° to 670° F.; the lowest temperature possible for the production of a good plate is desired. Some of the very skilful stereotypers in London actually cast the plate when the metal is of the consistency of thin gruel, and obtain the most exquisite results. It is not possible to give adequate written or verbal instructions in such work, it can only be done by the skill produced by long experience, and by the use of the most perfect alloys and equipment.

The latest development in the automatic casting of stereotype plates is by means of the "Winkler" casting machines, the invention of a Swiss engineer.

This machine is designed to cast the plates and at the same time to dispense with the "tails," the use of pumps, the necessity of trimming and shaving, and the preheating of the casting box. The casting box is connected directly to the melting pot, the metal entering by gravity through a long slit, which is opened and closed by a very ingenious valve in the form of a rod with twin bevils the whole length of the plate; the operation of closing severs the casting from the supply

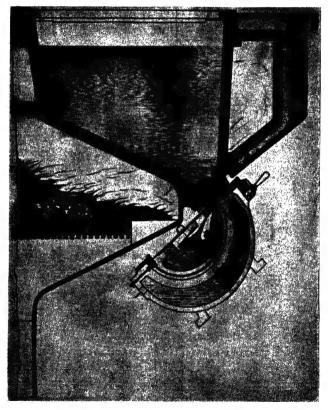


Fig. 14
WINKLER MACHINE, SECTIONAL VIEW SHOWING METAL
BATH AND PLATE IN MOULD

of metal, the "feeding" during the solidification is maintained from the full pot, under the natural pressure of the head of metal.

The melting pot is wedge-shaped, and the mouthpiece or slit is at its lowest portion. It is insulated by means of firebrick, asbestos, and siliceous marls, and the temperature is maintained for a long time after the source of heat is shut off. The surface of the metal is well protected, and is maintained in as non-oxidizing an atmosphere as possible. The plate mould is water cooled, and so, too, is the core or mandril, the control of water admission being automatic. The cock cannot be opened until the casting-box is effectively closed, thus avoiding splashes of hot metal.

The heating is by coal or coke, by gas or by electrical means, or by a combination of these. The electrical method of heating is greatly favoured, as it lends itself so completely to automatic control. The heating elements are immersed in the metal, and all external application of heat to the pot or container may be avoided, thus eliminating the danger of cracked pots to a very large extent. Effective thermostats are fitted. An electrically-wound clock, which is set to any desired time, switches on the current and starts the heating operation, so that the metal may be thoroughly molten and ready when the operators commence work. This is an attractive feature of this equipment.

# CHAPTER VI

#### SOLDERS

THE use of solders is almost universal in all industries which involve the use of metals.

These alloys are of necessity chiefly employed in the sheet metal and plumbing trades, but electrical and mechanical engineers and many manufacturing crafts use solders extensively. Further, there are indeed few amateur craftsmen who have not done a bit of soldering with more or less success. The very phrase "tinkering about" suggests the exercise of the art of the interesting and well-known "travelling tinker."

There are many grades of solder on the market, but the typical ones are represented by the following—

	Tin. Per cent.	Lead. Per cent.
1. Tinmen's or fine solder (sometimes called blowpipe solder)	69.0	37.0
2. Medium solder (largely used for tin plate work)	50	50
3. Plumbers' solder	33.3	66.6

Actually the percentage of tin is frequently found to be lower than stated in each grade, unless prepared to a strict specification.

Tinmen's solder has a melting point of about 180° C., considerably lower than that of either of its constituent metals.

The method of using it need not be described, but a few of the principles of this simple yet sometimes exasperating operation may be noticed as interesting.

In order that the solder may flow properly upon the surfaces of metal to be joined, the area must be heated to approximately 180° C., the melting point of the solder.

This is sometimes effected by the mere contact with the copper soldering bit, or soldering "iron," as it is generally called. The metallic surfaces must be clean, or the solder will not adhere. It is preferable previously to "tin," that is, to coat the surfaces with tin, before attempting to make the actual junction. A flux is almost an essential to the perfect cleanliness of the metallic parts. This is usually of zinc chloride, and is frequently made by adding scrap zinc to strong hydrochloric acid until completely saturated or neutralized. As hydrochloric acid is sometimes called spirits of salts. the flux is frequently termed "killed spirit"; sometimes a little ammonium-chloride or sal ammoniac is added. The function of the flux is to dissolve the film of oxide which forms at the temperature of the soldering operation. Other substances used are resin, or resin oil. oleic acid, etc. These bodies reduce the oxide if formed and make a protective film, so to speak, washing the metal surface clean at the increased temperature. The use of zinc chloride is by far the most common, but it is not permissible in some circumstances; traces are liable to be left behind, due to neglect or carelessness. after use, and this is found to act disastrously upon some goods when it comes in contact with them. Thus, it is customary to pack certain fine silken fabrics in tin or zinc lined cases for export. Traces of zinc chloride, presumably from unwashed soldered-joints, have been known to do much damage.

This is perhaps more common in the case of soldered zinc sheet than tin plate. The former operation is more troublesome, and raw acid is used as a flux. Acting strongly upon the metallic surface, it becomes zinc chloride, in situ. This work should always be thoroughly cleansed after completion.

Plumbers' solder of two parts lead and one part tin,

with possibly 1 per cent of antimony (this is by no means essential) is the most interesting of the series of solders. It has a long period of solidification. Freezing of some portion of the constituent alloy begins about 60° C. above the final solidification of the eutectic, which occurs at about 180° C. The plumbers' wipe joint, which depends upon this phenomenon, is the most commonly known example of the usefulness in practice of a long distance between solidus and liquidus.

It is customary to call the solders which consist mainly of tin and lead, and have comparatively low melting points, soft solders.

The whole subject of solder has been closely investigated during the past year by a devoted band of metal-lurgical workers under the auspices of the British Non-Ferrous Metals Research Association. There have been, in addition to this, considerable independent researches undertaken by great manufacturers and also by the staffs of departments of metallurgy in the Universities.

The information which has been furnished as a result of these investigations on the properties has greatly supplemented the knowledge previously obtained by experience in workshop practice.

The two impurities found in commercial solders are antimony and copper. Usually the amount of copper is very small indeed, and does not seriously interfere in the working or modify the physical and mechanical properties. If really appreciable proportions of copper are included in the solder, they become evident in the surface, and the alloy is liable to rejection. Certainly the experienced worker would soon recognize the appearance of 0.2 per cent of copper, both in the surface and the obstinacy in working.

Antimony is, however, another matter; it has gradually become recognized that a small quantity of this SOLDERS 71

metal does no harm, and it is sometimes claimed that some improvement is noticed when small quantities of antimony are included. Official specifications are sometimes found to prohibit more than 1.0 per cent, others preclude it altogether, whilst many tacitly permit up to 2 or 3 per cent.

The investigations, which have been conducted with so much care and attention to details, go to prove that with even 6 per cent of antimony of the tin content the physical properties in a 63 tin, 37 lead alloy are not adversely affected. It is, in fact, stronger and stiffer than the pure tin-lead alloy. Other tests are still being conducted. It is quite possible that objection may still be made to the presence of substantial amounts of antimony, on account of the slightly increased difficulty in carrying out the soldering operation. This is negligible in the case of small experimental jobs, carried out by skilled operators, in conditions where speed is of no great consequence, but, in cases of mass production with partly-skilled labour, the ease and rapidity of working become a much more serious factor.

It is interesting to note that the particular properties of tin towards antimony when alloyed are maintained in association with lead in the high grade solder. Tin is able to dissolve about 7 per cent of its weight of antimony, and to retain this amount when solidified in what is called solid solution. This amount of antimony cannot be detected in an etched specimen under the microscope. Any increase in this amount is easily detected in the form of the well-known cuboid crystals, and these conditions are reproduced almost exactly in the solder. The author has prepared specimens of solder containing gradually increasing amounts of antimony, and subjected the structure to microscopic examination until the critical proportion was reached

no antimony crystals could be seen until about 7 per cent of the tin present of antimony had been added. Beyond that amount the cuboid crystals were, in all cases, very evident.

The experienced worker can, however, detect spots on the surface of solder, when impurities occur, and for that reason much care is taken in the preparation of the alloy; an inspection of the mirror-like surface of a test ingot is the usual means of judging quality when purchasing supplies.

These means of assessing the value and judging the relative purity of metallic alloys are still very largely employed in commerce, in spite of the ready means of chemical analysis and assay now available. Tin is largely judged at the metal exchanges by a test of this character. There are, however, many pitfalls, and the expert who buys and sells on these tests is really backing or chancing his personal skill to a great extent.

It is strange that the surface spots which are considered to be objectionable in fine solders (those of high tin content) are not looked upon with such disfavour in the case of plumbers' or coarse solder, that containing approximately 66.6 per cent of lead and 33.3 per cent of tin. Here the spots are sometimes desired by purchasers, but the indications are not really reliable, as they may be produced by several causes.

The operation of soldering is so familiar to almost everyone, and probably the number of amateur workers who have obtained personal experience in soldering has increased threefold since the growth in popularity of wireless apparatus and experiments.

It would be altogether unnecessary in these circumstances to attempt to give instructions in the art of soldering; the skill worth having is obtained by practice and experience.

The temperature for soldering must of necessity depend upon the class of operation and solder employed, and not one person in a thousand has any idea of the temperature he is using, but that does not mean that he is unable to make a joint. It is found that about 275° C. is the actual temperature at which the best joint with a good fine solder has been made. This is the result of a series of very careful experiments. But it should be observed that this temperature is much above the melting point of an alloy of 63 per cent tin and 37 per cent lead, which becomes fluid at about 180° C.

Very careful and elaborate experiments have been carried out by the Non-Ferrous Metals Research Association in regard to the mechanical and physical properties of these solders, the effects of small quantities of impurities being strictly observed. The results of these researches are most important and useful. It is sometimes urged that, as the operations are carried out under ideal conditions as regards skill and time occupied, and also with the best equipment, the results are not comparable with those obtained in the workshop, with manufacturing conditions. This is not really so, for the commercial worker is amazingly skilful, and commercial conditions are now frequently better than those which obtain in the laboratories of colleges. Further, the possibilities are demonstrated by actual work and rigorous test.

Fusible Alloys. Fusible alloys can be manufactured with any desired melting point from 60° C. upwards.

The best known is Wood's alloy, which is made up as follows, its melting point is about 65.5° C.

Bismuth					per	cent
Lead	•		•	25	22	**
Tin .	•	•	•	12.5	,,	20
Cadmium				12.5	**	**

Until recently the chief use for these alloys was in the manufacture of sprinklers for use in case of accidental fires, and similar services, and for fusible or safety plugs in boilers, etc.

The introduction of wireless apparatus into so many households has, however, made many thousands of persons familiar with Wood's metal, as its low melting point makes it suitable for securing the detector crystal into its seating.

Other typical fusible alloys are-

	Compos	ITION.		
Lead. Per cent.	Tin. Per cent.	Bismuth. Per cent.	Cadmium. Per cent.	Melting Point.
26.7	13.3	50-0	10-0	60 to 68° C.
26.0	14.8	$52 \cdot 2$	7.0	68·5° C.
28.6	14.3	50.0	7.1	70·0° C.
27.6	10.3	27.6	34.5	75·0° C.
35.1	20.0	35.3	9.5	80·0° C.

The addition of mercury still further lowers the melting point of these alloys.

# CHAPTER VII

#### TIN PLATE

In the present days, owing to the popular and widespread dissemination of general knowledge, it is unlikely that many people make the old common mistake of thinking that tin plate consists of a sheet of metallic tin; it is in reality a thin sheet of steel coated with a skin of tin—steel for strength, tin for protection. The discovery of the method and principle of making this combination is one of the great achievements of man. It is not so striking or sensational as many of the great inventions which are epoch-making, but nevertheless it has had a profound effect upon the comfort and convenience of mankind, and its economic influence is almost incalculable.

The use of tin as a protective coating was in practice before 1620; the secret of the process was brought to England about 1670, and works were started in 1673, which failed. In 1720, however, Wales established the industry, was exporting by 1776, and from then onwards began to supply the world.

In the old days iron sheets were always used, the high grade material being termed charcoal iron, as it was prepared in furnaces in which charcoal was employed as a fuel and a reducing agent. Iron so prepared being free from sulphur was much more ductile and malleable. The cheaper varieties involved the use of iron sheets, in the preparation of which coke was used, and the product was less free from impurities, which lowered its mechanical properties.

The terms "charcoal plate" and "coke plate" have

been preserved in the tin plate industry and trade to the present, and will probably remain much longer. But the terms now refer to the general quality, for both "charcoal plate" and "coke plate" in their original reference to the iron of which the sheet is composed are obsolete terms, for steel sheet has almost entirely displaced iron plate for the whole work.

The great tin plate works of our country are closely associated with the steel industry, and command the highest grade products, and the result of the experimental work of the best metallurgical brains, together with the keenest and most skilled craftsmanship.

The rolling and preparation of the plates constitute a branch of steel works practice which cannot be described at length in these pages; the process, however, must be just noticed. The plates of iron or steel are prepared from bars, rolled and cut to about 15 in. long and 6 in. wide. These are heated and rolled until the width is increased to 15 in.; again heated and rolled in the opposite direction until it is about 51 ft. long. The plate is then sprinkled with coal dust to prevent it from sticking together, doubled, reheated, and further rolled between smooth rollers. This process is again repeated until the plates are reduced to the correct thickness or gauge. The details of the process vary to some extent in the various districts and works, but the principle remains constant, and, thanks to a fine spirit of co-operation amongst manufacturers, great uniformity and standardization, both as regards gauge and description, prevail throughout the trade. This, of course, necessitates a large measure of uniformity of production.

The sheets when they come from the rolling mills are termed "black plates"; they are then pickled in warm dilute sulphuric acid and scoured with sand and water to remove the scale of oxide of iron. The next operation is annealing; the sheets are packed closely like sheets of paper into a cast-iron box, and heated to redness in a gas-heated furnace. They are not removed suddenly from the furnace but are wheeled forward into the flue end of the furnace and allowed to cool slowly in a non-oxidizing atmosphere.

They are now coated with only a very thin film of oxide of a purple colour.

Subsequent further rolling and annealing sometimes take place, and a final dipping in sulphuric acid and a last scouring to obtain a perfectly clean metallic surface to receive the tin coating.

The plates are now plunged into baths containing molten tin, the surface of which is covered with palm oil or melted tallow, and thence on to simple mechanical devices which remove the superfluous tin and produce a clean and perfect surface. In some special cases reimmersion into the molten tin bath takes place. A very important operation now follows—the examination and sorting; for high grade work the sheets must be absolutely free from blemish or spot. These spots, which occur from time to time, despite the utmost precautions, lower the value of the tin sheets considerably, although they need not of necessity cause their rejection altogether.

The spots just mentioned are usually tiny untinned areas, generally due to little air bubbles in the bath of fluid metal. These bare spots constitute a danger in the subsequent use of the sheet.

This becomes more apparent if the reader considers for a moment the chief reasons for the use of tin as a protective coating.

Iron easily rusts or oxidizes, and thus rapidly becomes perforated or eaten away. It is also easily attacked by

organic as well as inorganic acids and corroding salts. Many gases also readily attack iron, but tin is not nearly so readily attacked; hence the great value of the coating. If, however, small areas are left uncoated or ineffectively covered, the bare patch and the surrounding coated portion become, in the presence of any corrosive fluid such as fruit juice, a galvanic couple, a very mild one to be sure, but sufficient to produce a continuance of the corrosion and the final destruction of the vessel or container into which the tin sheet has been made.

The careful inspection mentioned is therefore necessary. The perfectly satisfactory ones are now ready, and are packed in boxes, sometimes the plates separated by sheets of tissue paper to prevent scratching, and are sent to all parts of the world. These plates are termed primes, and when coated with an extra thick deposit of tin are described as charcoal, as a sort of mark of superlative excellence, although, as has been shown, the term charcoal plates had originally another meaning.

The plates which are found to have slight blemishes or uncovered spots are termed "wasters." They are entirely segregated, but are eagerly bought up by jobbing tin plate workers, who can easily cut up the sheets and reject the small defective spots, using only those parts which are perfectly coated.

There are even degrees of "wasters," termed "waste waste." These can still be used honestly by judicious cutting and selection, and are, of course, sold at lower prices than the ordinary wasters. The fact that such variations in quality may occur, and occur without the slightest implication of deception or fraud, emphasizes the urgent necessity for purchasers and users to select carefully their supplies from dealers who can be relied upon to include only the correct grade and description required.

The splendid reputation which the Welsh tin plate manufacturers have earned is based upon the excellent quality, the absence of variation, and the regularity in thickness of coating, of the various grades of product placed upon the world's market. There was at one time a great amount of secrecy observed. There is no need for this, yet there is a secret, not in the principles or the process of manufacture, but in the skill and conscientious work of the operators. Up-to-date and efficient plant and machinery, first-class material, modern methods, and scientific control, necessary as they undoubtedly are, fail unless they are backed up and supported by that fine craftsmanship which is apparently so instinctive as to give colour to the tradition of hereditary aptitude and the possession of family trade or craft secrets.

The extension of the power of productiveness of man has, to a great degree, been dependent upon the use of implements. The rude implements of stone displaced those of wood; in turn these were rendered obsolete by the employment of copper and then of bronze. The employment of bronze tools and implements marked a distinct period of advancement in civilization: the particulars of the growth of the Bronze Age, as it is sometimes called, and the part tin played in this chapter of the world's history, will be noticed in a later portion of this little work. Passing from the period of bronze implements we arrive at the age of iron and steel.

The Present Age of Engineering Construction. Let us examine for a moment the influence this simple article of commerce and general utility, tin plate, has exercised on the economy of life, through these stages, and its far reaching effect on the well-being of mankind in the present circumstances of the twentieth century. In the old days, food was produced and consumed locally. A comparatively small number of the products of the

harvests of the world could be enjoyed by people living at any considerable distance from the regions in which these harvests were gathered. This was true as regards the fruits of the earth in a great measure, but, as to the harvest of the sea and in some respects the animal world, transport was so difficult that decay rendered the food unserviceable excepting in such cases as dried and smoked meats and fish, and in some fruits and grain.

The use of tin plate has made it possible to effect packing, in clean, innocuous containers, hundreds of varieties of food stuff, whereby they may be transported in a wholesome and fresh condition for the use of nations and people thousands of miles distant, and to preserve for the use of mankind these foodstuffs in a serviceable condition for long periods. Thus the people in densely populated countries, and those living in places where the cultivation of crops or the production of food in any adequate manner is prohibitive, are able to obtain and enjoy the products of the earth to an extent which is difficult to appreciate properly, even when we are familiar with details in everyday life.

It is now possible to obtain the character of food to which one is accustomed, and which has become almost necessary to the individual in any part of the world, simply because it is made possible to preserve and pack it for transport, in air-tight and germ-proof containers of tin plate.

An exile in a strange land can sit down to a meal made up of dishes such as his family at home are eating an Englishman at Christmas can eat his roast turkey; an American his pork and beans; an Italian his spaghetti; a Spaniard his olives, and so on. The canned food is perfectly fresh and nutritious; the pleasing flavours and appetizing aromas are retained. Yet many months may have passed since the products were placed in their

safe covering of tin plate. A famine or a temporary dearth of food in any region of the earth soon provides an example of the possibility of rapid transport of food in relief of the distress, made practicable by this effective air-proof packing.

No more striking illustration of the value of tin plate for the conveyance of food stuffs can be referred to than the work of the Royal Army Service Corps during the War, in the provision and transport of food. Despite the inevitable criticism, frequently of a humorous character, of the commissariat department, there is no doubt that food of the right kind, in abundance, demanding no particular care in handling, easily served out, requiring the minimum transport space, retaining the natural salts and juices under very varied conditions of storage and distribution, was not merely one of the first essentials to the troops, but was a striking feature, which seldom failed, and which kept our men in extraordinary good health, and further relieved the desperate condition of the people of the countryside to an extent which no one who was not actually present can imagine. In the old days the armies had to live upon the country where the military operations were going on. In the Great War the conditions were often entirely reversed, for the villagers frequently subsisted almost solely on the soldiers' rations. In the earliest days after the army of occupation entered the country of the enemy, the troops found themselves billeted in houses where the women and children were almost in a state of starvation. the natural feeling of bitterness and hatred of the British soldiers was quickly turned to pity, and there is no doubt that the mess rations, and anything else which could be begged or even stolen from the Quartermaster's stores went to the relief of the families of the men whom we had so recently been endeavouring to kill most

th I whole

effectively. How far the packing of food in tin plate contributed to this state of affairs can be easily guessed. Without doubt the effect on all parties was a beneficent one.

It would be inappropriate to include in a little work of this character long lists of figures, or to load it with statistics, but it is interesting to note that the United States of America exported during the year after the War foodstuffs in enormous quantities. A few typical examples may be given, thus—

Salmon and other tinned fish	£7,000,000 worth
Meat .	£8,000,000
Vegetables	£2,300,000
Fruit .	£8,000,000
Milk .	£30,000,000
Infants' food	£1,000,000

The Dominions and foreign food-producing countries exported very large quantities, in proportion. All of this packed in tin plate, and, as the output of tin plate of our own country, notably South Wales, has the highest reputation, and deservedly so, it will be seen that the importance of this industry cannot be overestimated; moreover, the industry deserves the greatest attention and consideration from the whole empire and the authorities.

When we pass from the undoubted influence which the productions of the tin plate industry have upon the source of human power and energy: the food of the people, the next natural step is the source of mechanical power—Fuel. Here, of course, our own country has held a natural pre-eminence on account of our great resources and our undoubted skill and experience in mining, and, of course, our splendid shipping facilities. The growth of a second type of fuel has, however, become of immense importance, particularly during the last

quarter of a century-liquid fuel. Oil. Petrol. The man of even middle age can remember the period when the subject of liquid fuel was one talked of only amongst specialists and enthusiasts; the average person never thought of oil as a source of power. Life without petrol or some of its analogous fluids, for use in the engines of our motor cars, omnibuses, air craft, motor boats, etc., can hardly be imagined at the present time. And the distribution of petrol cannot be easily imagined without petrol-tins; certainly the great oil companies have established many distribution stations where one may fill the petrol-tank, almost as one watered the horses at a horse trough or the village pump in the old days, but the petrol-can still remains the stand-by of the careful traveller on the road. The transport services during the War used thousands of tons of tin plate in the form of petrol-tins alone.

Whilst thinking of the great users of tin plate, who naturally order in bulk great quantities for packing on the large scale, one is apt to overlook the ordinary householder who uses tin plate utensils of great variety. Tin pots, kettles, pans, and commonplace articles without number, undoubtedly these in the aggregate consume more of this universal material than any other single class of manufacture.

There is also another important class of plate called terne plate, humbler than the tin plate. It is made of the same steel sheet, but is coated with an alloy of tin and lead. It is therefore not suitable for use as containers for food stuffs or similar purposes, but for paint drums, and services of that character it is excellent. It is used largely in certain chemical works, and also in refrigerator plants.

Tin plates and terme plates are manufactured in a variety of sizes and gauges, many of which are standard;

but, within limits, sizes and gauges can be manufactured to suit customers' requirements.

All measurements and prices are based on the area of the standard box of tin plate. 20 in.  $\times$  14 in.—112 sheets which is equal to 31,360 superficial inches, weighing 108 lbs. These are called I.C.

Plates thinner than I.C. are called lights. The variations most usual are 100 lbs. and downwards in gradations of 5 lb. to the box. Plates thicker than I.C. are called crosses. As this matter is often quite a mystery to the ordinary user, the details are given.

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Basis 20 in. × 14 in., 112 = 108 lb.—

IXL = 122 lb.

IX = 136 lb.

IXX = 156 lb.

IXXX = 176 lb.

IXXXX = 196 lb.
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Odd sizes and thicknesses can, of course, be produced, but the designer or manufacturer who desires his production to be carried out with reasonable economy (and who does not in these difficult times?) should endeavour to arrange for his requirements to come within the range of standard sizes and weights.

Tinned Foods. The following extract from The Wellington Journal will be of interest to everyone—

"In the ordinary way there is not much risk in the use of tinned foods; it is, however, just as well to be careful, though the tendency of most of us, in opening a tin, is to be over-suspicious. The sense of smell is not always a sure guide as to the soundness of the fruit, fish, meat, or whatever it may be. The contents of a tin should always be sweet; even a slightly unpleasant odour or a 'soapy' taste will indicate that something is wrong. If, when opened in the dark, the contents exhibit any glow of phosphorescence, the tin should be rejected.

In the process of canning, the tin is first filled with the preparation and the top, which contains a small hole, is soldered on to the body.

"After the air is driven out, the small hole in the top is soldered up. Providing the air has been properly excluded, the contents will keep good for years, but it is important to see that the tin has not been punctured. If air has been left in the tin or the preparation not sufficiently sterilized, a gas will be produced, and the pressure of this gas inside the tin will cause the top and bottom to bulge—a sure sign that the contents are unfit for consumption. The contents of any tin should not, of course, be allowed to remain after it has been opened, but should be placed in a dish and consumed as soon as possible."

Dr. W. J. Melhuish, D.Sc., Ph.D., an authority on the subject of tinned foods, has pointed out that salmon, which is of high food value, and similar commodities come from a land of plenty, the purity being thus guaranteed, as there is no temptation to pack inferior goods; and there is in all the great packing organizations a system of splendid inspection, together with a standard of cleanliness of the highest order.

The same authority advised the abandonment of solid shelving for storing in shops and warehouses, and the adoption of narrow strips, separated, which allows free circulation of air round the goods in stock, and prevents accumulation of undesirable matter.

The printing upon the surface of metallic tin, either for pure tin articles, such as collapsible tubes, or upon tin plate for containers of all descriptions is a very important matter in modern commercial practice.

The makers of printing inks or colours for use on tin are well advised to become possessed of a lithographic press, and to retain the services of a skilled lithographer. Further, it is wise to install a special arc lamp, designed to enable the operators to detect fugitive colours under varying conditions of light and heat. The neglect of these precautions is apt to lead to much disappointment and loss, for colours which appear in the ordinary way to be perfectly suitable, either are found to be comparative failures under the necessary storing temperatures, or fade hopelessly under the strong actinic light of the sun or the ultra violet rays.

Offset printing is largely employed in printing on tin plate, and, as the film of colour is often extremely thin, the best possible colours or inks should be used.

At one time it was thought that opaque colours only should be used for tin printing, but this is by no means so. Vermilion is a good opaque colour, and stores well; fast geranium and alizarine (these are actually dyes obtained from coal tar products) are transparent by comparison, but they are largely used with success.

Whites used for foundation work are very opaque, but many yellows, lakes, etc., are fairly transparent.

Easy working of tin printing inks is an essential feature. Easy running, a smooth finish, elasticity, and good drying are of the greatest importance. Elasticity, even when perfectly dry, is a feature which cannot be over-estimated, and it is one which is very closely allied to the drying property. It will be readily understood that a printing ink or colour which will dry satisfactorily on paper or other absorbent substance may well be a very slow and unsatisfactory drying covering medium, on an impervious and smooth surface, such as is presented by metallic tin.

The drying function is not a perfectly simple one. On paper there is some absorption, some evaporation, and some oxidation which causes the linseed oil and the gum varnish to produce a fine, thin film or skin. In tin

printing the absorption is absent, the rapidity of the process includes a steady evaporation, and, when the oxidation is too rapid, the skin or film is apt to be brittle, so that cracking and chipping of the printed surface results. The printing ink, which is somewhat similar in character to artists' colours, must possess a balance of these properties in such a nice degree that the drying shall be rapid, the film hard, yet retaining a certain toughness and elasticity which shall permit the tin plate or pure tin article to be bent and handled more or less severely, without the risk of injury to the coating of colour or print. Driers are sometimes added to the inks during manufacture; in fact, a certain proportion is always present, but, in the highest grade work, and by the most experienced craftsmen, special driers having just the right amount of oxidizing agents, with a proportion of toughening constituent, are added at the commencement of the operation, the amount and character varying according to the job in hand, thus ensuring the requisite elasticity which is so desired, but which is so elusive.

The insides of tins used as food containers are sometimes required or desired to be lacquered, or coated. An anti-acid, non-poisonous, gold lacquer has been produced for this purpose, and is known under the registered name of "zinnatine." It is the invention of Messrs. Holden & Son, Birmingham. Pasteurizing varnish, as well as special varnish which is flexible enough to withstand deep stamping, and weather-resisting coatings can be supplied for covering the sheets of tin intended for subsequent operations.

Undoubtedly the Welsh tin plate trade is one of the most virile in the country, it has passed through many critical periods, and yet it has been able to withstand the high tariffs and the severe foreign competition.

On the authority of Messrs. Brooker, Dore & Co., the trade is stated to have grown from very small beginnings to 18,000,000 boxes a year, of which the home trade takes about one-third.

Owing to improvements in manufacture and the reduction of the amount of tin used, the cost of production has come down very materially. The lowest recent price at which the standard box of  $20 \times 14$  has been sold is 19s., and in the boom period of 1921 the price rose to 80s. basis, the present value being 23s. 6d., or nearly double what it was in July, 1914, just before the outbreak of war.

Unfortunately the price of steel in this country is too high compared with the cost on the Continent, and Germany, from being a good customer, has become a competitor; prices in that country being about 15 per cent lower than they are here.

So far American competition has not seriously affected us, but the works in that country have taken some Italian and South American contracts from us.

In one week in December, 1924, the following shipments of tin plates and terne plates were made from South Wales ports: Cardiff, 591 tons, Newport, 115 tons, Swansea, 8,894 tons, making a total of 9,800 tons as compared with 6,669 tons during the week immediately preceding.

### CHAPTER VIII

## TIN PLATE TRADE IN INDIA

THE great importance of tin plate manufacture is so manifest that it has impressed itself upon the authorities throughout the world. A very important step has been taken in the establishment of a large and very complete works in India. This step has made a great impression and, at a recent meeting of the American Iron and Steel Institute, a paper was contributed, entitled, "The Manufacture of tin plate in India," by Mr. Frank L. Estep. This paper attracted great notice and was reported in many of the Industrial Journals. As it constitutes a good description of an up-to-date factory, and the considered requirements of the industry of tin plate manufacture, an abstract of the paper is given.

The works are at Jamshedpur, and are owned by the Tin plate Company of India, Limited. Their erection was carried out largely under the supervision of Mr. F. L. Estep.

The buildings are of special construction to ensure a maximum of air in the hot Indian climate. In addition, special provisions have been made in the hot mill to ensure continuity of operation regardless of temperature. Between the units of two double mills there is installed a fan of 36,000 cub. ft. a minute capacity, delivering 18,000 cub. ft. to the men on each mill through underground ducts. As it was not certain whether the men on the hot mills could stand up to their work better with a given quantity of hot dry air, or with the same quantity of air at a lower temperature with a higher humidity, each of the fans was installed with an air

washer on its suction. By this means any proportion of the total amount of air going to the men, from 0 to 100 per cent can be put through a spray and its temperature reduced. This proved to be a very wise provision, and Mr. Estep states that it was practically the salvation of the hot mill, so far as its continuous operation was concerned during the first summer season of 1923. Special provision was also made by installing an exceptionally large area of water-cooled floor plates for each mill.

Electrical power, three-phase 50 cycles, is supplied from the Tate Company's station, about 3½ miles away, over a loop line, at approximately 3,200 volts at the generator switchboard, which drops to 2,800 to 3,000 volts at the tin plate plant. The power house contains a 1,000 kva. 750 kw. 250 volt D.C. motor generator, and the motor driving the cold rolls, together with the gear reducing set and gear train.

There are also a motor-driven compressor and a direct connected oil-engine-driven 12 kw. D.C. generator unit for emergency use to generate direct current enough to operate main oil switches, when and if the power goes off the main line and shunts the plant down.

All A.C. auxiliary power apparatus is 440 volt, all cranes are D.C., and many of the individual machine tools, stoker drives, blowers, and all tinning machines are driven with variable-speed D.C. motors.

Transformers are located at various points for low tension voltage for lighting.

Clearing the site for building the plant was begun in January, 1921, but not much work had been completed before June, 1921, when about 35 per cent of the total volume of heavy concrete had been put in. About 4,200 tons of structural work and about 4,000 tons of machinery were erected, about 90 per cent of which had been

imported from England and the United States via Calcutta. The structural steel, together with the buildings for the Tata extensions, made a total of about 32,000 tons of made-up steel work: this was, at the date of the contract, the second largest amount of fabricated steel ever contracted for in the United States.

Construction had proceeded far enough to make possible the first attempt at starting one hot mill on 18th Dec., 1922, and the final and successful starting took place on 1st Jan., 1923. The second hot mill was put into operation four weeks later. Black plate was opened, stacked, and covered, and all energies bent towards completion of the rest of the plant. The annealing furnace was completed and put into operation and the first set of cold rolls started late in April, 1923, and the first run in the tin house on one machine was during the week ending 5th May, 1923. The second tinning machine was started during the week ending 7th July. The entire plant was completed in construction and ready to operate at capacity by 1st Sept., 1923, and between that date and 12th Dec., 1923, the remaining four hot mills were successfully started up, and the plant was in full operation one week less than one year from the date of the initial attempt at starting one mill.

In July, 1922, when it was hoped to start operations by about 1st Oct., it was decided to secure a works manager, and a hot-mill superintendent for this plant, who had experience on this type of mill in the United States. Two men were secured from the gang plant of the American Sheet and Tin Plate Company. For the remainder of the European or covenanted staff it was thought entirely practicable and advisable to secure experienced tin workers from Wales. A total of about 90 men were secured from South Wales. There were

54 experienced hot-mill men, 24 heaters, 21 rollers, and 9 helpers, making one full crew of eighteen men to a shift for one hot mill. It was further proposed, and all the men understood, that later on their duties would be not only to perform the work of rolling, heating, doubling, catching, etc., but that they should also use every effort to teach the native to do all the various jobs in connection with the hot-mill work. The remainder of the men from Wales consisted of foremen for various departments, such as bar-storage, shearing, and opening floor, pickling, annealing, cold rolling, tin-house, and warehouse; also mechanical engineer, electrical engineer, roll turner, millwrights, etc.

Rolling Mill. The hot-mill department consists of three units of two double mills each, one double mill on each side of the motor. Each unit is driven by a 1,000 horse-power American or 850 horse-power Indian rating, 3,000 volt 300 revs. a min. motor, through a reducing gear set with very heavy fly-wheels. The rolls are 28 in. in diameter, and run at 33.2 revs. a min.

The cold-roll department consists of four sets of rolls, three in tandem, the roughing train driven at 48 revs. a min., the intermediate at 50 revs. a min., and the finishing train at 52.6 revs. a min. from a 750 horse-power 3,000 volt, 500 revs. a min. induction motor through a gear reducing set and a train of five cut gears. Nine cranes together cover all operating departments, with the exception of the black pickling, and they range from 5 to 15 tons capacity.

The hot-mills were equipped with six Steele mechanical doublers for the roughers, and also with six with shears for the finishers. Experience has proved that, without the mechanical means of doubling, it would have been impossible to operate successfully during the hot months on the two-roll, three-part system in India. The physica

effort of hand doubling would undoubtedly have proved too great for the native workmen, Europeans would have been unable to stand up under the work during the hot months, and output would have dragged materially. Further, it would have entailed the importation of at least twice the number of European operatives for the hot-mill proper, and operating costs would have become prohibitive.

The black-pickling machine is of the grey type, built by Messrs. Taylor & Sons. Limited, of Briton Ferry. and is the latest design of this machine. The whitepickling and tinning is done on six Thomas-Davis white-pickling, tinning, and cleaning combination machines, manufactured in South Wales. These are installed in a building designed especially for them, and erected in such a manner that they are rights and lefts. with coal firing pits common to two machines, and so arranged that each machine discharges its tinned product directly into the warehouse for inspection. Each machine is completely hooded and connected to a separate stack which surrounds the tin pot stack. The draft was insufficient to pull out the heavy fumes and vapours, and suction fans were later on installed with each hood.

The hoods can be quickly removed by cranes, to permit stripping the pots during repairs.

Handling Material. The movement of material through the plant during the process of manufacture, from bars to finished tin plate, is as follows—

Bars brought in from the Tata company's plant near by are unloaded by a crane in the bar storage building, placed when wanted at the bar shear, where they are cut to the desired lengths. Cut bars are loaded on bar carriers, picked up by the crane, stacked on a truck, and weighed as they pass into the furnace building. Here the bar carriers are placed by a 5-ton crane at the back of the six continuous pair furnaces.

Coal is emptied into a large coal pocket from the track outside the furnace building, and a grab bucket on the furnace building crane delivers the coal into hoppers holding about 1½ tons each, and feeds the individual stokers by gravity. Ashes are collected in cars on an industrial track, which passes out across the yard through the enclosure wall, and are dumped in the neighbourhood of the return water pond.

Scrap from the mechanical double shears, as well as from the squaring shears, is collected in large steel buckets, carried with the mill crane or shear-building crane to a point opposite the scrap-baling press, which is located in an extension to the shear building. A 3-ton mono-rail hoist covers the baling-press pocket, and extends out of the building far enough to cover three railway trucks.

Black-plate is opened adjacent to the shears, placed on special carriers and conveyed by overhead crane to a point opposite the black-pickling building, and here placed upon small hand trucks. These trucks pass over a scale, and all plate leaving the opening floor is weighed as it enters the black-pickling department.

In operation of the black-pickling machine the crates make an elliptical movement into one acid and two water tubs, and at the discharge end of the circuit the crates are unloaded and the plates passed over the inspection benches, which are located directly underneath the crane runway, and then stacked, without further handling, on to the annealing bottoms in the black-annealing building. The plates are placed on false bottoms which set on the annealing bottom proper, and their use has proved of very great benefit.

After the plates are flushed with a hose and the bottoms

covered and sealed, they are picked up with a 15-ton crane and placed on a furnace car, at the entering end of the black-annealing furnace. After passing through the furnace for black annealing, the furnace cars are discharged on a transfer car at the other end of the furnace, which brings them back into the black-annealing building. When cooled, the annealing bottoms are unloaded opposite and in front of the cold rolls, and as the plates are cold rolled, they pass across the furnace building and are again stacked on annealing boxes at the back of the last train of cold rolls in the white-annealing building.

At this time and for the present capacity of the plant, the boxes, when loaded with cold-rolled plate, are transferred back into the black-annealing building. Later on, when a white-annealing furnace is installed, these boxes will pass through for white annealing in the same manner as is done in the furnace for black annealing except that the movement will be in the opposite direction, thus bringing the plates after white annealing out at the end of the white-annealing building opposite the cross building leading to the tin house. When properly cooled the white-annealed bottoms are picked up by a 15-ton crane, put on a car, and, after passing over a scale and being weighed, are delivered underneath a 10-ton crane in the tin house. This crane picks up each false bottom with its load of white plates, or the bottom with the entire load, and sets it down in front of either of the tinning machines. Here the plates are removed from the piles, are sanded, and placed in the feeding pockets of the tinning machines. From this point until they are picked up in the warehouse and placed on the inspection benches, the plates are not touched or handled, and, as compared with best existing practice, approximately five handlings in all

have been eliminated between white annealing and inspection.

The plates go through the Thomas & Davis machines in four streams for wide plates and eight streams for narrow plates, and are pickled, swilled, tinned, cleaned, collected on a cross conveyor at the discharge end of the machine, and brushed with rotary brushes. They are then changed in direction of movement 90°, again brushed with rotary brushes (this time at right angles to the previous brushing), discharged from this brushing machine on a belt conveyor which carries its load through a slot in the wall into the warehouse, where they are picked up in piles and placed on benches for inspection.

In the warehouse the plates are inspected, slit, counted, boxed, and sealed, and are held on the floor ready for delivery to Calcutta. It was originally thought it might be possible to do away with the sealed container and pack in wooden boxes, but, on account of the severe rains and moisture over several months of the year, it was finally decided to seal all deliveries and not attempt to use boxes.

In regard to the hot-mill rolls, the first shipment left the United States on 8th Oct., 1921, and the last shipment on 16th March, 1922. All these rolls had lain in the open at the works until the plant was up and the roll lathes ready to turn rolls. This ageing and slow annealing process has resulted in a very long life, and, up to 1st Jan., 1924, only five hot rolls had been broken. There had been rolled 31,721 boxes of black plate before the first roll was broken, and it had been gagged three times. All the other broken rolls had either been gagged, or had had tongs rolled, or both.

Output. The largest week's output of two mills was made during the week ending 1st Sept., 1923, when 15 shifts turned out 4,483 boxes, or 7.07 tons of sheared

black plate, practically all 182 in. × 56 in., 30 gauge. The greatest 24 hour output on two mills was on 7th Aug., 1923, when 995 boxes were made, an average of 166 to a mill to a shift. The third mill was put in operation on 3rd Sept., the fourth on 15th Oct., the fifth on 14th Nov., and the sixth or last mill on 12th Dec., 1923. The first full production to a mill to a shift was 132.9 boxes. For the entire year of 1923 there was hot-rolled a total of 213,940 base boxes, an average of 131.5 boxes per mill to a shift. The best total week's production on the hot mills for six mills was for the week ending 30th Aug., 1924, when a total of 12,910 base boxes was rolled in fifteen shifts, or an average of 143.4 boxes to a mill to a shift. Based upon the operation of the plant up to date, it is conservatively estimated that for fifty weeks' operation the plant will have a capacity of 600,000 boxes minimum to 700,000 maximum a year.

There were tinned during the year 183,080 base boxes, of which 143,838 boxes were "primes," 37,292 boxes of "firsts," and 1,950 boxes of "seconds."

The black and white pickling for the year was done with a consumption of 7 lb. of sulphuric acid, and the tin consumption was 1.69 lb. to a base box. The record up to date on two machines is 6,007 boxes made during the week ending 8th Sept., 1923, in 120 hours of operation; the best record on three machines was 9,038 boxes, made during the week ending 3rd Nov., 1923, in 117.7 hours of operation; and the best week's output on four machines was 9,754 boxes during the week ending 19th Jan., 1924, in 119.1 hours of operation.

The first delivery of tin plate was made to the canmaking factory in the latter part of May.

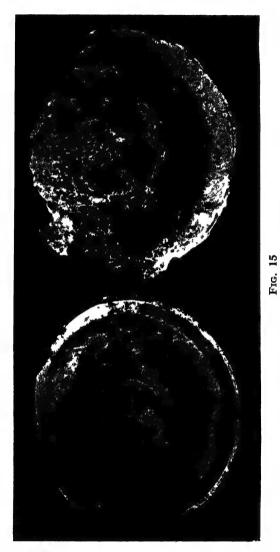
## CHAPTER IX

### PEWTER

THE ordinary student of metallurgy is usually taught that pewter is an alloy of 80 per cent tin and 20 per cent lead, with the slight modification to the effect that French pewter for use in drinking vessels is not permitted by the authorities to contain more than about 18 per cent lead, on account of the acid character of the wines of the country, it being stated that with larger proportions of lead the alloy is readily attacked, and risk of lead poisoning results.

The technical man who does not, in his work, come into contact with pewter to any serious extent, and further, does not study it for the sake of its artistic or antiquarian interest, is quite content to allow the matter to rest there, and does not inquire any further into the manufacture, composition, or history of this very interesting and beautiful series of alloys, or the ancient craft associated with it.

Modern technical literature gives little detailed information regarding pewter; in fact, compared with the alloys used in engineering and other construction, it may be said to be neglected to a very remarkable extent. Fortunately Mr. H. J. L. J. Massé has given us a splendid work on pewter plate, but this is only to be found in the libraries of the enthusiastic collectors, or in such libraries as the British Museum or the Guildhall. An excellent volume by the same author, entitled Chats on Old Pewter (unhappily the work is now out of print, and so editions are becoming rare) is available to the student and the enthusiast. To the collector or



ROMAN PEWTER FOUND AT APPLESHAW, HANTS.

8--(1463в)

the beginner who plans to collect old pewter for its own sake and the interest to be obtained from it, the advice is, study Massé, and be saved from many pitfalls.

The pewterer's craft was for many centuries controlled and protected by the Worshipful Company of Pewterers, and so far-reaching were the powers of this ancient guild that they employed searchers who were empowered to enter workshops and places where the craft was being



Fig. 16
PYX
(XIVth Century)

carried on and seize and confiscate or destroy articles, tools, and products which were not in accordance with the usages and regulations of the Company. Mr. Welch's *History of the Pewterers' Company* gives, with great wealth of detail, the historical and social story of the members of the company.

The author is indebted to these works for the notes on pewter, from a collector's point of view, without which a book, however modest, on tin, would be lacking in something which should be included.

Despite the strict regulations of the Guilds, it appears that no well-recognized specifications existed in the old times for the composition of pewter. It was always recognized as an alloy consisting mainly of tin, but the additional metals which were intended to give it special physical and ornamental qualities were generally left to the skill and ingenuity of the craftsman, with the result that many claims for special secrets were made. These were, of course, generally spurious, although not by any means intentionally fraudulent or false. As in many other crafts, secrets of manufacture exist in the skill and experience of the designer and craftsman.

These secrets cannot be stolen or even acquired without corresponding labour, diligence, and ability, whereas specifications as to composition of alloys can



Fig. 17
FLAGON
(Midhurst Church. Dated 1677)

be readily communicated, or even built up from the results of analysis of the final products.

Fine pewter consisted of 112 lb. of tin and 26 lb. of copper, these being the amounts taken for an ordinary charge or melt. Sometimes brass instead of copper was

introduced, making a further complication in composition on account of the 30 per cent of zinc present in the brass.

It is so customary for modern metallurgists to consider all compositions of alloys in percentage proportions that it will be readily seen that the proportions taken by the old craftsmen, when reduced to parts per cent, make irregular and somewhat eccentric figures, which



Fig. 18 CHALICE AND PATEN

give a fictitious sense of mystery to the amounts of the various constituents.

Other comparatively commonly met alloys were tin, 100, antimony, 16; or tin, 100, antimony 17; and an alloy, named after its maker, Pemberton's alloy, tin, 90, antimony, 10.

Common pewter consisted of tin, 82 to 83 per cent and antimony, 17 to 18 per cent. These alloys are white and hard, durable, capable of taking a reasonably good burnished surface, and of retaining it under careful handling and condition.

Lead has at all times been a common constituent with tin in pewter, some Roman examples being found to consist of 70 tin, 30 lead. The commoner varieties of English pewter were found to contain 20 to 25 per cent of lead, the remainder being tin, and it is this alloy which, being generally met with in commerce, gave the simple formula generally known to the present day metallurgist. For it is much more likely to be subjected to chemical analysis than the special varieties employed in valuable pewter vessels or artistic objects

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the sampling of which is always a matter of extreme difficulty. The scientific metallurgist generally finds the collector very difficult and obstinate, when it is proposed to scrape off sufficient metal to make an adequate analysis, although the collector has generally raised the question of the composition himself. This is, of course, perfectly understood, and sympathized with, but the present day scientific man has little faith in the old time method of judging the composition by scratching, appearance of surface, touch, and similar devices.

These methods, which naturally find great favour with experts, connoisseurs, and collectors, are so strictly personal, and cannot well be shared equally by all, that the articles are apt to be judged in conditions which differ, and according to different standards.

Bismuth is sometimes added to the alloy, so that one occasionally finds pewters consisting of tin, 90, antimony, 7, copper, 2, bismuth, 2, which, unfortunately, make up 101 instead of 100, and it is presumed that the extra one part is expected to be lost in the process of melting.

As bismuth is extremely like antimony in its physical features, it is presumed that the early workers generally employed it to reduce the melting point of the alloy, particularly of the dross or metallic scum which consists of finely divided metal and oxide.

The Continental pewterers did not use much antimony. Fioravanti employed 88 per cent tin and 12 per cent lead for dishes and porringers. The French pewterers used smaller proportions of lead. Modern French craftsmen use larger proportions of lead, but the amount is still kept rather low on account of the acid character of the wines, and the danger of lead poisoning, due to the formation of lead acetate or sugar of lead, which, being readily soluble, is a dangerous poison.

In some cases zinc has been added. Ashberry metal

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is an instance of a zinc-bearing pewter, consisting of 77.8 per cent tin, 19.4 per cent antimony, and 2.8 per cent zinc. This casts very well, and is hard and wears well.

During the last few years the composition of pewter has been more or less controlled by the Board of Trade. Naturally the standard is a fairly high one, and 10 per cent of lead is recognized as the maximum. It is not certain that this or any other specification is strictly enforced in a legal sense, but the absolute recognition of a good standard, the compulsory stamping of the vessels used as measures, and the authority of a Government Department backing the whole proceeding, is a very excellent feature of the present day practice. The very inferior and rich-lead pewters, particularly public house drinking vessels, are becoming obsolete, and good class workmanship and material seem likely to be recognized once more in this fascinating craft.

Britannia metal is a modern and special variety of pewter, and should contain no lead.

Massé gives the following proportions as typical of good specimens of Britannia metal—

Tin.	Antimony.	Copper.	Zinc
150	10	3	-
140	5	2	-
90	8	2	
85.7	10.4	1	2.9
81.9	16.2		1.9

The special creaking or cry, or cri, of tin, caused by the crystals of the metal grinding together, noticed when a stick of tin is bent is mentioned in the earlier chapters. This feature is of considerable value to the collector of pewter, and much attention is paid to it in judging the quality and relative purity of the alloy.

Zinc is generally supposed to spoil this cri, and lead to a lesser extent. The modern metallurgist, however,

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mistrusts these signs, as he knows from experience that quite a pronounced cri can be obtained from a high grade solder, which contains over 30 per cent lead.

It is to be sincerely hoped that the fashion and consequent demand for good quality pewter may revive and greatly increase. It cannot be altogether cheap



Fig. 19

# GERMAN TANKARDS (Seventeenth and Eighteenth Century)

on account of the high cost of tin at the present time, and this is to some extent an advantage, for there is not much temptation to put inferior design and workmanship into good and comparatively costly materials.

Messrs. Liberty are now encouraging the manufacture of English pewter, and much of the work now shown in their picturesque establishment gives promise of a real revival of a love for good work. It is stated that 95 per cent tin is guaranteed in all the articles now being produced in Liberty's works in Birmingham. It is

very probable that ere long the substantial and artistic character of these productions will gain in favour and to some extent displace the fashion in thin and flimsy silver, or in cheap and nasty electro plate. This remark, of course, applies only to that class of electro plate of the most inferior type.

One particular use to which pewter has long been put, which is quite different from the ornamental arts usually associated with the alloy, is the production of music plates, that is, plates upon which is engraved the musical score and used for printing.

This metal, like the black-metal of the public house tankard, seems to have fallen from grace, as regards composition, for the lead content has increased to an alarming extent. A plate which the author examined a short time ago, on which the engraving was perfect, consisted of tin, 27.3, antimony, 3.4, copper, 0.6, lead, 68.7 per cent. On the other hand, a very common looking public house tankard yielded on analysis 97 per cent of tin, the remainder being antimony with only traces of copper and lead.

A series of samples obtained from scrap pewter sold simply for the metal, the whole series of consignments being hopelessly damaged and of no value from a collectors, point of view, gave figures as under—

	Tin.	Antimony.	Copper.	Lead.
A	50.3	2.2	1.0	46.5
$\mathbf{B}$	91.0	4.4	1.3	3.1
C	56.2	6.2	1.2	36.3
$\mathbf{D}$	59.5	1.1	Trace	39.3
E	44.3	3.4	0.9	51.2
$\mathbf{F}$	79.4	7.4	1.3	4.9

(F was a sample from a Galway collection)

The Manufacture of Pewter. The answer given by a really great authority on pewter, to the question "How is Pewter made?" is "By the traditional methods" (by

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melting the alloy and casting it into moulds). This is a very inadequate description of the first and highly important item in the manufacture of the alloy, for, when it is considered that tin, the main constituent,



Fig. 20 MODERN PEWTER (Liberty)

melts at about 230° C., and copper at well over 1,000° C., whilst antimony has a melting point of nearly 640° C., it is fairly obvious that some special steps should be taken to avoid the serious overheating of the bulk of the tin, whilst dissolving the more refractory copper and

antimony. This is effected by making intermediate rich tin-copper and rich tin-antimony alloys, which melt at much lower temperatures than the means of their constituents, and are fairly readily dissolved in a bath of heated tin, or better far by pouring them in a molten state into the bath of tin.

It would be inappropriate to discuss the metallurgical technicalities in a chapter on pewter, but it should be noted that it is not a simple mixture or even a solution of the individual metals, but of several constituent alloys which have different melting points, and which solidify in successive stages, the whole finally being cemented together by a fairly definite alloy called the eutectic. These facts were not noted with much precision by the early workers, chiefly because pyrometric observations were not possible; but undoubtedly many of the ancient craftsmen knew much more of the physical properties of the alloys at elevated temperatures than we are disposed to credit them with; this knowledge, obtained by experience, became a part of the "trade secrets" which at one time were valued so highly.

After the casting of the alloy into ingots, it was ready for re-melting; for all good metal mixers make more than one melting in making up alloys.

The metal is then re-melted and cast into moulds. The moulds were either what are now called chill moulds, or dies, that is, permanent bronze or iron moulds, or in plaster, sand, or similar material.

The permanent moulds are in many cases two, three, or more part moulds, the various sections being carefully fitted and dowelled together so that the portions could be taken apart to release the casting. The better the workmanship in the fitting of the various parts together, the less trouble is encountered in connection with fins of metal showing on the casting at the position of the

joints. Much skill is frequently shown in the selection of the position of the joins, so that trimming of the casting shall be possible on a part which is of small importance.



FIG. 21

MODERN PEWTER

(Liberty)

After the casting is completed the next process is cold working, to use a modern phrase, really hammering or spinning, the latter operation being performed by pressing a hard tool upon a rotating sheet or disc of metal, usually in the lathe. The old-fashioned method of

forming was carried out entirely by hammering, and in the later methods the spun articles are frequently finished by hammering, the marks being left upon the finished article.

Finally, the pewter articles, if required to be finished smooth and bright, are burnished.

The casting is required to be carried out with great care, and the moulds are carefully heated, to avoid too sudden chilling of the metal before the mould is filled. The inner surface of the moulds is coated with ochre or oxide of iron, china clay, or some such finely powdered substance mixed with gum or white of egg.

The greatest precautions are necessary to prevent the entrance of dross or scum into the casting.

Frequently candlesticks and similar objects are cast in several pieces when required in fairly large numbers, the various parts being afterwards assembled and very carefully soldered together.

Undoubtedly carelessness and neglect have been responsible for the loss of much pewter which is valuable, not only for its beauty, but also for its antiquity and its historical associations. It is not particularly liable to damage, it merely tarnishes by exposure to the air, and in many respects this tarnish, or patina, adds to, rather than diminishes its value to the collector, and the lover of old objects of fine craftsmanship. Pewter is not to any serious extent corroded in ordinary circumstances, nor is it subject to disintegration known to modern metallurgists as age hardening or age cracking. The cleaning of pewter is a subject which has exercised the expert and enthusiastic for centuries past, and many recipes are given for special scouring mixtures.

Such bodies as Calais sand and elm leaves are prescribed. The first question which is suggested is, "Why Calais sand?" The answer is probably two-fold; it PEWTER 111

is most likely that the worker was French, and the nearest sea sand available was at Calais. Sea sand is a very sensible suggestion; it generally consists of rounded grains, like microscopic pebbles, the absence of sharp corners thus avoiding the scratching tendency of sand from a sand pit, or sharp sand. Possibly the worker considered that the sand from the shores at Calais became more thoroughly rounded in form, due to the action of the sea at the narrow Straits of Dover.

The plant equisetum hiemale was said to be known in some localities as pewter-wort, as it contained a considerable amount of siliceous matter in its shoots.

Fine emery powder, crocus powder, rotten stone, and similar abrasives may be used.

For modern methods a composition of soap and kieselguhr is generally employed. Polishing-bobs, made up by fastening together a large number of discs of calico into a sort of wheel, are made to rotate very rapidly on a polishing lathe, the speed being upwards of 2,000 revs. a min.; a piece of the polishing composition is held to the edge of the calico wheel; and then the article to be polished is pressed lightly or strenuously against the wheel. Much care and judgment are required, or any valued marks or engraving are rapidly removed, if the article be applied to the "polishing-bob" with too much pressure.

Much care should be taken to remove any of the polishing materials from the joints or hinges of pewter vessels, as this is a fruitful cause of loosened joints and the subsequent loss of a portion of a vessel.

Dents in hollow vessels and in plates should be treated with great care, for the skilled craftsman seems to have a sort of intuition as to the position where the blows should be applied when hammering out these dents or bulges. The beginner should watch a skilled person before attempting operations of this sort; the blows always seem to be effective when applied in the most unlikely places. Thus a bulging part is usually straightened out by hammering round the bulge, not upon it, for if the latter course be adopted the plate becomes still more drawn or extended in the part which is already too much thinned, and the bulging is accentuated.

It is pointed out by Massé that one of the commonest causes of damage to pewter vessels of the tankard class is the provision of feet, such as ball feet or lions couchant as feet, as gradually the bases bulge. These feet are sometimes added to embellish the vessels, and the thickness of the bottom is not sufficient to sustain the weight of contents. In any case the broad flat bottom should be allowed to remain.

Apart from the charm of the possession, and the fascination in the act of collection and selection, which really becomes a species of gentle sport, the study of the laws and customs of the craftsmen and the companies controlling their trades is particularly engrossing. From Roman times the workers in pewter have been held in some measure of esteem, and specimens of their handicraft many centuries old are occasionally discovered, and some may be seen in various collections and museums.

The craft seems to have suffered in mediaeval days owing to itinerent workmen travelling round the country recasting and repairing specimens, doubtless often spoiling valuable articles. Various guilds were formed and, in the reign of Edward II (1348 according to Riley), the Pewterers' Company became officially recognized. Restrictions were put upon the making of the alloy, and inspectors and searchers were appointed with powers to confiscate inferior goods and to prosecute the workers who engaged in unlawful practices.

The training of apprentices was regulated, and underselling discouraged. Further, the social and moral well-being of the members of the craft was safeguarded. Neither lock-out by masters nor strikes by workmen were permitted.

As an outcome of these rules and regulations, a high standard of workmanship and material was established, and the rivalries, which, of course, existed, were the estimable result of competition of artistic craftsmen.

In order that the makers of articles and the place and period of origin should be identified, distinguishing marks, signs, and initials were stamped upon the finished work. The study of these marks, or "touch marks" as they are termed, has become the subject of much research and discussion amongst the experts. Records of these marks are kept and referred to when any fresh or doubtful specimen is discovered.

The Worshipful Company of Pewterers has a wonderful collection of these touch marks. Mr. Massé has made an exhaustive analysis of these, together with other records, which greatly enriches the amount of information available on the subject. The illustrations in a beautiful work by Mr. Malcolm Bell, also out of print, are such as greatly to charm the collector, and to suggest the subject as one worthy of study by anyone with a fair amount. of interest in metals and craftsmanship.

## CHAPTER X

#### TIN FOIL AND TUBES

The application of the metal to the manufacture of tin foil or the compounded foils of tin and lead does not at first appear to be of outstanding importance, but it is of much greater dimensions than the casual observer would imagine. Including the employment of metal for the manufacture of collapsible tubes, the annual consumption of tin for this industry in our own country alone runs into hundreds of tons. To a considerable extent both the metal foil and tube trade are luxury ones. The price of ingot tin will almost certainly regulate the demand for both classes of goods.

In the cases of pure tin foil, it is generally admitted that this is the best wrapper for confections, although aluminium foil is now a somewhat formidable rival, due almost, if not entirely, to its lower price, because in other respects it is apparently not altogether suitable.

Recent comments by one of the greatest authorities in the collapsible tube business indicate that these tubes are used mainly for tooth pastes, rubber solutions, liquid glues, and artists' colours. It can be said that for several years now the market has been a buyers' one; and it is very much a question if the industry is not one of those where competition has already been carried beyond the limit within which it is healthy, and of advantage in the end to the prospective purchaser.

Collapsible Tubes. There are two classes commonly in demand which are prepared almost wholly or partly from tin—the pure tin and the tin-coated varieties.

The first group is prepared from the purest Straits

tin obtainable, i.e. Banca or Billiton, to which is added a fractional percentage of antimony or other suitable hardening constituent; the second category comprises tubes made from metal consisting of a lead core to which has been attached, by a cold rolling process, a tin sheet, the percentages composition by weight allowing generally for about 1 per cent tin coating each side of the lead sheet. It is interesting to note that Herbert, with his new type of hardness test, in which he employs an apparatus described as the Pendulum Tester, has obtained indications that the tin coating prevents the work hardening of the steel core in the case of tin plate, and that independent investigation in the U.S.A. establishes the same point in connection with tin coated lead-foil. These results of observations of scientific workers naturally give rise to much discussion in technical circles. If Herbert's observations are supported by continual experience of the manufacturer, the point is one of great technical importance. The case of the absence of work hardening of the lead core is of less moment, for it is held by many authorities that pure lead does not harden by cold working, but that an actual softening can be detected.

Probably the most interesting feature in the process of manufacturing these tubes is the fundamental operation of extending the body, shoulder, and nozzle of the tube in one pressing operation from a disc or dump of varying and special shape. The length of engagement between the forcer and die is quite small, and the tube is squirted out of the space between the two at a rate of flow which the eye can just follow. To the uninitiated this operation is always impressive.

Many, if not the major portion, of these tubes are highly decorated, the usual procedure being to apply first a white or coloured enamel background on which is printed, in suitable harmonious colours, a fancy design and any type required. Lip salve cases and also sprinklers for perfume bottles are also manufactured in a manner which is almost identical with that just described.

The caps for the tubes are formed from "dumps" either by a capsuling or pressing operation. They are of all varieties, from the simple plain type with a sunk milled edge, to the regal crown cap. The comparatively plastic nature of the metal permits of its being readily formed into quite complicated shapes.

Metal Foil. For the wrapping of confections in this country the purest tin foil is used exclusively, the various mixed or composition foils being extensively adopted, on the other hand, in the tobacco industry.

Naturally, for the former purpose, purity is a first consideration; the arsenic contents particularly should be the minimum possible. Fortunately the antimony in this tin-rich alloy is in solid solution with the tin, so that it cannot, as has been proved by experiment, contaminate in any way the food stuff or sweetmeat for which it constitutes a seal or wrapper.

When it has been said that these pure tin foils are commonly required six to seven thousandths of a millimetre in thickness, it is easily appreciated, especially by those experienced in the rolling of metals, that satisfactory results can be obtained only by constant attention to metallurgical and other manufacturing details.

For the polishing of this foil, steel rolls which are very hard indeed, actually having a scleroscope hardness of about 100, ground and buffed to a perfect mirror finish, are employed. This refers to the modern method of rolling; where the sheets are reduced to the required gauge by rolling in packs, a former common practice,

the slip between adjacent sheets produces a natural polish.

There is now an increasing demand for all the highly decorative lines of tinfoil. The variations possible in the colouring, embossing, and colour-printing of the foil are many. With brilliantly coloured lacquers the most effective results are obtained, and it is not the least interesting thing to find how closely the lacquer can be made to adhere to the highly polished metallic surface. On certain coloured backgrounds, again, bronze printing can be applied to produce most attractive results.

In the trade, "gauge" refers to the covering capacity of the foil, not, as is more usual, to the thickness of the sheet. It will perhaps convey an impression of its thinness to say that foil having a covering capacity of about 13,000 sq. in. per lb. is very much used in the confectionery trades. If one excludes gold leaf, this must rank among the thinnest of foils.

The composition of mixed foils, i.e. those consisting of tin and lead, ranges from comparatively thick tincoated lead, having perhaps 1 per cent of tin in the core and ½ per cent to ½ per cent of tin on each face up to a 95/5 alloy, the first figure indicating the nominal tin contents per cent. As might be expected, the minimum thickness obtainable increases in moving from the tin rich to the lead rich end of the series.

In the preparation of these foils the chief defect met with is minute perforation in the finished sheet. It can well be imagined that, with sheets as thin as those mentioned, complete immunity from "pinholes" is not easily attained.

Tin foil is used in certain rather delicate processes by the stereotyper and electrotyper. For this work sheets of considerable area being required, the greatest care is demanded from the operators, and, in fact, all who handle the sheets. The operation in which the foil is used is similar in principle to that which we were all familiar with in our school days, in taking impressions of coins in tin foil or silver paper, as it was frequently called.

A very unusual and extraordinary use for tin foil is its introduction into big guns, or ordnance, before firing, a very small quantity being added with the charge. It is stated that it does much to prevent or diminish the deposit of copper on the rifled bore of the gun, derived from the copper driving band, the thinness of the tin foil presenting the metal in the required state of fine division, and thus facilitating the interaction of the metals with the necessary rapidity.

## CHAPTER XI

#### DIE CASTING

A BRANCH of engineering manufacture which is at once most interesting and of growing importance is that known as die casting. It is difficult, if not impossible, to give a comprehensive and descriptive definition of the process, but as so many of the articles in everyday use are made by the methods which are included in the term, and as the process is reducing manufacturing costs and increasing output to such an enormous extent, it is appropriate that a brief description of this relatively new system of metallurgical production should be given.

The process may be said to consist of a method of producing castings by pouring or forcing molten metals and alloys into highly finished moulds or dies, these dies being of metal, and therefore of a permanent character, and distinguished from the usual form of sand moulds with loam cores usually employed in the foundry.

The dies are formed in such a way that articles cast in them are practically finished, and require little or no machining. Extreme accuracy as to dimensions and form is attainable, and holes, recesses, screw threads, both internal and external, are completed in the one operation of casting.

Many of the industries which are referred to in this work employ the principles of die casting, notably the type caster, in all the varieties of his calling. Probably the first notable case of die casting on a large and organized scale was the production of the linotype machine, where rows of type cast into one slug, the length of the line of print required, were produced by

mechanically forcing molten type metal into a mould which was capable of opening and releasing the finished casting.

There is quite a competition between two industries as to which employed die casting first—the bullet caster or the type caster. Certainly both of these crafts were engaged in the earlier half of the last century.

But the process has extended its usefulness to a very considerable extent, and now not only metal of the type metal character is cast in permanent moulds, but aluminium alloys and even brass and aluminium bronze are employed. As will be readily seen, these alloys of higher melting point are much more destructive to the metal dies and moulds, which have a correspondingly shorter life than those employed in casting metals which have a lower melting point. This is not the only difficulty to be contended with, but it is the most obvious one, and, in fact, the principal one.

The metals chiefly employed are zinc, tin, antimony, and lead, with small proportions of aluminium and copper.

The great increase in the production of much wireless apparatus has been made possible at a reasonable cost by the application on a large scale of die casting. Gramophone parts, optical instrument details, electrical fittings, and many articles of domestic and common use are produced in a practically finished state by casting directly into the highly finished dies of steel. Screwed cores for internal threads, and collars and bushes which are removable for external threads, make it possible to cast threads without showing the line of join of the die, whilst movable rods and pins ensure the formation of holes of standard position and dimension, with a degree of accuracy up to a correctness of less than one-thousandth part of an inch.



DIE-CASTING MACHINE CLOSED READY FOR OPERATION

At one time it was customary to distinguish between the system of casting by gravity, that is, simply pouring the metal into a mould from a ladle, and the method of forcing it into the mould by a mechanically operated pump; the former being called chill casting, and the latter die casting. The higher metallurgical authorities, however, made the latter definition cover the whole field of work with permanent metal moulds.

Pressure work is very difficult with the metals of higher melting point, whilst the alloys of tin, zinc, antimony, and lead lend themselves well to it.

For production on a large scale, zinc base alloys are in the greatest demand.

A typical alloy is as follows-

Zinc.	Tin.	Copper.	Aluminium.
85%	8%	4%	3%

In some cases the tin content is considerably higher, and frequently the aluminium is lower.

Castings in a finished condition are produced in alloys of this class in many thousands a day. They are strong, hard, and durable, the movable cores permit a great variety of design.

The metal is of relatively low melting point, and it is essential that the contraction shall be well defined and controllable; also that it shall not have too severe action upon the metal of the mould, and that, in order to make really good, sound, and sharp castings, its constitution shall be such that it has a period of plasticity. When fluid, it must be mobile and the tendency to oxidize too rapidly shall not be pronounced. These features have made it possible to obtain a finish in many respects quite equal to machined parts, with a hard skin and great accuracy as to dimensions.

It is largely claimed that the castings may be produced by unskilled labour.

This claim must not be accepted without serious qualification, for it is the experience of the best engineers engaged in this work that the operators obtain a very high degree of skill, and that money saved in this direction is not true economy.

The design and manufacture of the dies or permanent moulds demand the greatest possible skill and much practice and ingenuity; in fact it is difficult to speak too highly of this branch of the work. Good men are necessary in every department: in no part is the job a "fool-proof" one. The experience in this work is similar to that obtained in the majority of mechanical processes of modern manufacturing practice: that operations which are looked upon as capable of being performed by "any old labour" seldom pay.

The temperature of casting must be watched with great care. If too low for the particular alloy, little folds and creases appear on the surface of the casting, and, of course, one has the ever present danger of defects through a partially filled mould. If the temperature be too high, one gets splashing, long fins, and oxidation.

The moulds are generally made in mild steel, which must be well forged and free from surface defects or inclusions, for any irregularity of the surface is certain to be reproduced on the casting. Alloy steels are used for special work, but the manufacture of the dies is such difficult work, that fairly easily worked steel is preferred, and these special steels used only when absolutely necessary. Cast-iron is used in the body of the dies when possible.

There are many refinements in the art of tool making, which cannot be described well in this account, but none

is of greater importance than the arrangements for venting the mould.

It will be readily seen that the air contained in the die, as well as any gas in the molten metal, must have a chance of getting away, before the actual solidification of the metal. The dies being of steel, no air can escape through the material of the mould as in the case of ordinary sand moulds. Thin flat spaces, only a few thousandths of an inch in thickness are provided, communicating with the interior of the mould. This allows for the ejection of the air and prevents splashes of metal.

The skill and discretion used in placing the vents and adjusting the movable cores are among the great secrets of present day die casting. They are secrets which cannot be communicated, for they are the result of the experience and skill of the die designer; and every fresh job demands special and individual treatment. The moulds are frequently water-cooled, hollow spaces being provided for the circulation of water, during the working operation. The alloys used are zinc-base, tin-base, lead-base, and aluminium-base, and finally copper-base alloys. The base metal is that which preponderates largely.

As mentioned in the beginning of this chapter zincbase alloys are largely used. And a typical composition is given. The varying constituent is usually tin. It has been found necessary to increase the proportion of tin up to 18 per cent in the case of some very difficult work in zinc-base alloys. This lowers the melting point and prolongs the plastic period.

A typical lead-base metal is-

Lead. Antimony. Tin. Copper. 80% 15% 4% 1%

But all the varieties of type metals may be used.



Fig. 23
DIE-CASTING MACHINE IN OPERATION

Of the tin-base metals, high tin bearing alloys are used more in die casting operations than any others; all the grades described under the title of white bearing metals can be employed.

Other tin-base metals especially adapted to withstand the action of gas, for valves, are—

Tin. Antimony. 60 to 90% Remainder

High tin content, or the presence of low melting point tin rich constituents, must be considered in cases where the articles have to be stove-enamelled, or it will be found that tiny beads of alloy liquate out from the surface.

The machines in which die casting is carried out vary greatly in design, but are fairly similar in principle. Usually they consist of a metal pot with suitable burners to maintain the metal in a molten condition; the melted metal is generally supplied by ladles from an external melting pot. Attached to the metal pot is a pump, which is actuated by a lever; communicating with the nozzle, the die is brought into contact with the metal supply, and fastened very firmly by suitable clips, so that no metal may escape in splashes when the pump is operated. The upper and lower portions of the die are usually jammed together by a toggle joint, which operates very quickly and firmly, extra clips and securing screws being used for large castings.

The machines shown in the illustrations are those used at the works of Messrs. Fry's Metal Foundry. In these the metal enters the die in a vertical direction, the plate holding the die being swung, on a hinge, away from the metal pot after each casting.

This type of machine is used in this country, although a horizontal machine is also favoured, particularly in the United States.

#### CHAPTER XII

#### ASSAY AND ANALYSIS

A FAIRLY common request among users of tin alloys and others interested, is for a quick and reliable method of assay or analysis of tin bearing ores, alloys, and residues, in order to estimate the value and the tin contents of such bodies.

It has been stated in preceding pages that the work is highly technical and hardly suitable for a small general work such as this, but in order to give the reader an idea of the methods employed, or to indicate to those who have the necessary experience and skill in assaying and analysis, a few of the methods which are used by those who are constantly engaged in this work, the following notes are added.

It should be needless to emphasize that competence in assay and analysis cannot be obtained from any book. Nothing can take the place of training and experience gained by systematic practice.

It appears simple to instruct one to weigh, filter, and wash a substance, but no one without laboratory training can appreciate the importance and difficulty in carrying out these apparently simple operations without loss of some of the material which is being handled. Such loss which may easily escape ordinary observation would vitiate the accuracy of the analysis and probably lead to an unprofitable transaction.

Sampling. No operation in connection with the assaying or analysis of material is more important than sampling.

The whole object is to obtain a sample which is fairly

representative of the bulk. No matter how refined and accurate the assay or analysis may be, the result is misleading and worthless if the sample does not truly reflect the average content of the parcel of ore or metal under consideration.

In the case of ores the whole of a large representative sample should be crushed and thoroughly mixed. It is then made into a conical heap, divided into four portions or quartered, two opposite portions mixed and the quartering repeated, and so on until a suitable amount is obtained for assaying. This procedure is also adopted in the case of residues, ashes, or metallic compounds which are required to be valued by assay.

In the case of alloys, the sampling has of necessity to be varied, but the precautions to ensure the provision of a thoroughly representative sample must be equally rigid.

To obtain a sample from a pot of molten tinny alloy, the fluid metal should be thoroughly stirred and a portion withdrawn in a small ladle and cast in a button mould. This is repeated several times during the emptying of the pot, so that not less than three buttons are obtained, sawings from these are taken, mixed, and used for the analysis. It may be necessary to remelt the mixed sawings under oil, and take a final sample with the hack saw, the finely-divided metal being carefully freed from iron by a magnet.

The reader will appreciate from the earlier description of alloys of white metal such as antifriction alloys, printing metals, and similar bodies, that as the ingots cannot be perfectly homogeneous, it is fatal to take chippings from either the top or bottom only of ingots for valuation by analysis. Drillings or sawings should be made right through the ingot, these remelted carefully, cast into a button, and this sawn for final sample.

Once more let it be thoroughly understood, sampling must not be left to a casual or inexperienced person. It may appear superfluous to add that the sampler must also be honest and reliable in every respect.

The cost of a parcel of tin-bearing material, whether of ore, metal, or workable residue, naturally depends upon the amount of tin contained or recoverable. A sample showing a too rich content would therefore inflate the price beyond its proper value and also place the works under the serious charge of losing the valuable metal in the processes of reduction and refining.

When it is remembered that the margin allowed to cover the cost of the working processes of the metal recovery and refining is small (this margin being sometimes termed the "returning charge"), it will be understood that a loss of 1 or 2 per cent in the anticipated yield will absorb the expected profit and convert a seemingly paying operation into a serious loss.

The principal object of an assay is to determine the amount of metal which may be expected to be obtained from the ore when it is worked on the industrial scale, rather than to determine the exact amount contained in the ore. The latter information is also desired so that the efficiency of the extraction processes may be ascertained and checked.

The total metallic content of the ore can be learned only by a wet assay or analysis of the ore, whilst the assay as first mentioned is by a dry assay, or a part dry and part wet process. It is desired that the process shall, in as large measure as possible, copy the industrial process to be employed in the extraction.

Assay of Ores at the Mines. The method generally employed is that called Vanning. In its most elementary and simple form it consists of washing the sand and earthy material from the black tin. The operation is

carried out with a shovel and a tub of water, much skill and dexterity being exercised by the operators or vanners.

The process appears to be somewhat rough, but remarkably accurate results are obtained by experienced workers, or rather the assay figures give a very close approximation to the results obtainable from the large scale practice.

The degree of fineness of the ore influences the result. Thus, if the cassiterite be in granular form the loss is not considerable, but if it be crushed to a very fine powder, or if it contains a large proportion of powder, the losses, in the form of slimes, become serious.

For this reason vanning cannot be used with success in assaying slimes or tailings from the dressing processes.

Concentration. The ore to be smelted and to be assayed is concentrated so that it contains not much less than 50 per cent of metallic tin, though it is desirable that the concentration shall be as much higher as possible.

A weighed quantity of the concentrate, 80 to 100 grms. is intimately mixed with about one-fifth its weight of powdered anthracite, which is called culm, then placed in a blacklead crucible, loosely covered and heated to a white heat for about 20 minutes. The crucible is gently agitated to collect the particles of reduced metal, which is poured quickly into an ingot mould. The crucible and residue are carefully examined, and any remaining particles of metal are, after cleaning, added to the ingot and weighed with it.

Borax is frequently used with the anthracite, as this assists in making the slag more fluid and promotes the collection of the metal in one lump.

The reduced metal is remelted, cast in a solder mould in stick form, and examined for indications of impurities. A bright mirror-like surface is desired; on the other hand, a frosty surface points to the presence of some traces of other metals. The experienced assayer can read the signs with remarkable accuracy, and can decide if a more elaborate chemical analysis is necessary.

Cyaniding. Another method which is frequently employed in the assay of concentrates is to reduce the oxide of tin with potassium cyanide. The concentrated ore is also sometimes treated with nitric acid, or a mixture of nitric and hydrochloric acids, to remove impurities; sometimes it is fused with bisulphate of potash and washed with water, and finally with ammonia to remove traces of tungsten compounds.

The acid treatment involves risk of loss of tin by solution, consequently the acid washings must be carefully examined for tin. In using the cyanide reduction, the ore and cyanide are both finely powdered and about 20 grm. of each are well mixed and heated in a crucible, at first gently, and afterwards more strongly, in order to collect all the beads and particles of metal; it is then poured into a mould in the form of a button.

The button is cleaned by remelting with borax, or under palm oil, and weighed. There is usually some loss of tin in the slag. It is usually found necessary to make occasional chemical analyses of the button of tin, for traces of antimony, arsenic, lead, and other impurities, but, as before stated, the appearance of the surface is to the experienced metallurgist a fairly safe indication.

Wet methods of assaying tin ores, or processes involving the solution of the tin contained in acids, are very difficult on account of the insolubility of cassiterite in acids.

In order to effect solution it becomes necessary to reduce the insoluble oxide to metallic tin. This may be done by heating to dull redness in a tube furnace in a stream of carbon-monoxide, hydrogen, or coal gas, or

<sup>10-(1463</sup>в) 12 рр.

by heating with finely-divided zinc, magnesium, or aluminium. There are many other special devices employed by metallurgical chemists with this very obstinate form of tin oxide.

Gravimetric Method. One other method should be mentioned—heating with sodium hydrate to a red heat. The tin oxide is converted into a soluble stannate of sodium. Porcelain or silica crucibles must not be used for this fusion. Metallic tin in the form of drillings, sawings, or other fairly small particles is attacked by diluted nitric acid. The stannic nitrate which is produced decomposes on boiling, and a white precipitate is formed, this is insoluble, and is called metastannic acid. It consists of tin dioxide and the elements of water. This inter-action forms the basis of the simplest gravimetric method of estimation of tin in alloys.

Estimation. To ascertain the amount of tin in a sample of gun-metal or solder (free from antimony) weigh carefully 1 or 2 grm. of the alloy in the form of sawings, place in conical flask or beaker, add about 15 cub. cm. of strong nitric acid and a small quantity of water. Boil, taking care there is no loss by spurting. Add water with a little acid if necessary, boil for about 20 minutes or until the residue is quite white. Break up the precipitate or residue with a rounded glass rod, dilute and filter. The soluble metals, copper and zinc in the case of gun-metal, or lead in the case of solder, are dissolved and will be found in the filtrate.

The white residue on the filter must be washed very thoroughly, first with very dilute acid, and finally with water until quite free from metals other than tin. Dry the paper and precipitate, detach with great care, place in weighed porcelain crucible, burn paper, add ash and any adhering precipitate to contents of crucible. Heat

to redness until all the contents are quite white when cool. Weigh, deduct weight of filter ash and of crucible, and calculate the dried precipitate as SnO<sub>2</sub>, multiplying by .7867, and the result gives amount of tin. Calculate percentage. If antimony be present this method cannot be adopted, as the antimony will largely, but not entirely, remain with the tin and be weighed as Sb<sub>2</sub>O<sub>4</sub>.

Tin is sometimes estimated by precipitation by sulphuretted hydrogen in the form of stannous sulphide, in an acid solution of chloride of tin. This is employed when it is desired to separate other metals; a more or less detailed description of one of these processes is given below.

The sulphide of tin is filtered, washed, dried, and converted into oxide by heating. Care is required to avoid loss by volatilization in the earlier stages of heating. The oxide is weighed and the amount of tin calculated as before.

Clarke's Process. Moist, freshly precipitated sulphide of tin dissolves in a strong solution of boiling oxalic acid, and a process for the separation of tin sulphide from antimony and arsenic sulphides is based upon this property.

A solution containing tin, antimony, and arsenic as chlorides is saturated with oxalic acid, the liquid is kept boiling, and sulphuretted hydrogen is bubbled freely through it for about 30 minutes. The oxalic acid prevents the precipitation of the tin, whilst the sulphides of antimony and arsenic are thrown down.

These are filtered off, the solution containing the tin is made alkaline with ammonium hydrate, then ammonium sulphide added, the sulphide is precipitated and redissolved in excess of the reagent, acetic acid is now added to decompose the solution, and tin sulphide is antimony. Fit the flask with a tight rubber bung, fitted with a Bunsen valve, boil the solution for 10 minutes to reduce the tin. Close the valve quickly on withdrawing flame, and cool the solution as much as possible without admission of air. Add 5 c.c. starch solution and titrate with standard deci-normal iodine as rapidly as possible.

1 c.c. 
$$\frac{N}{10}$$
 iodine = .00595 grm. Sn.

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